THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 12, NUMBER 4 APRIL, 1944

The Mercury Photosensitized Polymerization of Acetylene *

D. J. LE ROY AND E. W. R. STEACIE
Division of Chemistry, National Research Laboratories, Ottawa, Canada

(Received January 21, 1944)

An investigation has been made of the mercury ($^3P_1$) photosensitized polymerization of acetylene. The polymerization is inhibited by nitric oxide and it is concluded that free radicals are probably involved. The quantum yield of the uninhibited reaction is 4.5 ± 1.2. Experiments over the range 25°C to 300°C show that the temperature coefficient of the reaction is not large. A few measurements were also made with Cd($^3P_1$) and Cd($^1P_1$) atoms.

INTRODUCTION

RECENT investigations of the reactions of the lower paraffins and olefins photosensitized by Hg($^3P_1$), Cd($^3P_1$), Cd($^1P_1$), Zn($^3P_1$), and Zn($^1P_1$) atoms[1] have shown that the following reactions take place.

For the paraffins we have

$$M^*+C_nH_{2n+2}=C_nH_{2n+1}+H+M$$
$$\text{or}=C_nH_{2n+1}+MH, \quad (1)$$

and for the olefins

$$M^*+C_nH_{2n}=C_nH_{2n}^*+M, \quad (2)$$
$$C_nH_{2n}^*+C_nH_{2n}=2C_nH_{2n}, \quad (3)$$
$$C_nH_{2n}^*=\text{products}, \quad (4)$$
$$M^*+C_nH_{2n}=C_nH_{2n-1}+H+M$$
$$\text{or}=C_nH_{2n-1}+MH. \quad (5)$$

In the case of the olefins the particular reactions occurring were found to depend on the energy of M*. Thus for Cd($^3P_1$) (87.3 kcal.) and Zn($^3P_1$) (92.5 kcal.) reactions (2) and (3) were predominant. For Hg($^3P_1$) (112.2 kcal.) the important reactions were (2), (3), and (4), although (5) also occurred to a small extent. In the case of Cd($^1P_1$) (124.4 kcal.) and Zn($^1P_1$) (133.4 kcal.) reaction (5) appeared to be of greatest importance.

Since an investigation of other types of carbon-carbon bond systems was of some interest, measurements were made on acetylene, using Hg($^3P_1$) atoms. Previous work[2-4] has indicated that the polymerization proceeds by an excited-molecule process. Melville in particular has proposed an elaborate mechanism based on the reactions

$$Hg(^3P_1)+C_2H_2=C_2H_2^*+Hg(^1S_0), \quad (6)$$
$$C_2H_2^*+C_2H_2=(C_2H_2)_2^*, \quad (7)$$
$$(C_2H_2)_2^*+C_2H_2=(C_2H_2)_3^*, \text{ etc.}, \quad (8)$$

with chain-stopping steps of the type

$$(C_2H_2)_n^*+C_2H_2=(C_2H_2)_{n+1}. \quad (9)$$

* Contribution No. 1146 from the National Research Laboratories, Ottawa, Canada.

[1] See D. J. Le Roy and E. W. R. Steacie, J. Chem. Phys. 10, 676, 683 (1942) for a summary.

[2] J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. 49, 2438 (1927).

[3] J. C. Jungers and H. S. Taylor, J. Chem. Phys. 3, 338 (1935).

[4] H. W. Melville, Trans. Faraday Soc. 32, 258 (1936).

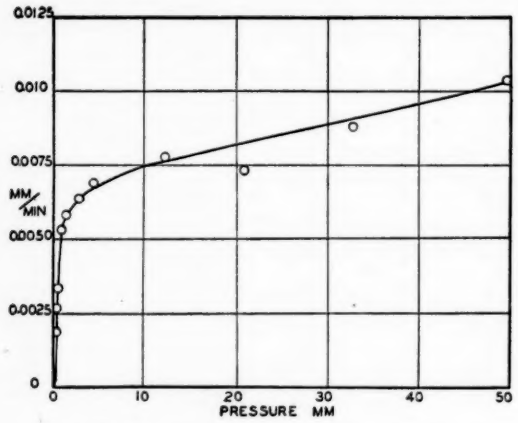


FIG. 1. Rate of pressure decrease *vs.* pressure, at 25°C (Series I).

Reaction (6) is analogous to (2), the important primary step in the reaction of $Hg(^3P_1)$ atoms with ethylene, but that is the only similarity between the two mechanisms. The analog of (5) was considered unlikely, but the evidence of the present investigation, indicates that this latter reaction is also possible.

EXPERIMENTAL

Some preliminary runs were made in a static system, but it was found that unless mercury vapor were continually supplied the rate fell off, indicating that mercury was used up in the reaction. Melville has made the same observation.

The system used for the temperature range 25° to 75°C (Series I) consisted of a fused quartz cell 6 cm in diameter and 5.5 cm long with plane polished windows. The volume of the system was increased by connecting the quartz cell to a large flask which was immersed in a thermostat and kept at 30±0.02°C. A pool of mercury was placed in the bottom of the large flask and the gas was continuously circulated over this mercury surface and through the system by means of a special pump using mercury as the piston. It was so designed that the volume of the system was kept constant, thus making it possible to measure pressure changes to 0.01 mm with the pump in operation. A magnetically operated valve kept the gas circulating in one direction. The total effective volume of the system was 1710 cc.

The mercury resonance lamp was immersed in the 30° thermostat and light entered the cell through a fused quartz window in the side. The cell itself could be surrounded by a smaller thermostat with a fused quartz window. Distilled water was used in both thermostats and the smaller one could be kept at any desired temperature. The concentration of mercury vapor in the cell was that corresponding to its vapor pressure at room temperature since the gas was passed through a U-tube at room temperature before entering the cell. With this apparatus there was no evidence of a falling off in rate other than that due to the accumulation of polymer on the wall. This was removed by flaming at the end of each run.

The system was changed slightly in order to investigate the reaction at higher temperatures (Series II). A smaller quartz cell was used (100 cc) and this fitted into an aluminum block furnace with a double-walled quartz window. By suitable adjustment of the wattage the temperature could be controlled to ±0.2°C or better. Thermoregulators of the saturated vapor type were used and found to be very satisfactory. The power supply was controlled by a vacuum-tube relay. As in Series I, the gas was passed through a U-tube at room temperature in order to fix the mercury pressure. At furnace temperatures above 25°C the actual concentration of mercury would be less due to expansion. The effective volume of this system with the cell at 300°C was 1580 cc.

Pressure changes were measured with a McLeod gauge up to 4 mm and with a Pearson gauge at higher pressures. In both cases the accuracy was approximately 0.01 mm.

Acetylene, drawn from a cylinder, was slowly passed through a trap cooled with dry ice to remove most of the acetone and further purified by a series of bulb-to-bulb distillations. Nitric oxide was prepared by the action of mercury on a two percent solution of sodium nitrite in concentrated sulphuric acid. It was purified in the same way as the acetylene and stored in a bulb fitted with a mercury cut-off. Analysis showed it to be of high purity.

Although a more complete analysis of the products will be reported in a later publication the method, briefly described, was to collect the

gas at atmospheric pressure in a thimble inverted in a small trough of mercury. This was greatly facilitated by using a small mercury diffusion pump backed by a Sprengel pump. In this way quantities of gas less than 0.02 cc were easily collected. The actual analysis was carried out with a Blacet-Leighton gas analysis apparatus. The procedure for determining nitric oxide is described elsewhere.[5]

A few runs were made using $Cd(^3P_1)$ and $Cd(^1P_1)$ atoms to initiate the polymerization. In this case the lamp and cell were mounted together in a somewhat larger furnace. A partition separating the lamp from the cell had a circular aperture over which was placed a Corex D window for runs with $Cd(^3P_1)$ atoms, or a quartz cell containing chlorine gas for runs with $Cd(^1P_1)$ atoms. The lamp itself has already been described.[6]

RESULTS

A. The Mercury Photosensitized Reaction

Effect of Pressure on the Rate

In agreement with Melville and with Jungers and Taylor it was found that the rate increased markedly with pressure at low pressures and then flattened off. Figure 1 shows the pressure dependence of the rate at 25°C. The falling off in rate at low pressures can be shown to be due entirely to incomplete quenching. With the stipulation that the chain length be independent of pressure the reaction at low pressures of acetylene can be expressed by the reactions

$$Hg(^1S_0)+h\nu = Hg(^3P_1), \quad (10)$$

$$Hg(^3P_1) = Hg(^1S_0)+h\nu, \quad (11)$$

$$Hg(^3P_1)+C_2H_2 = X. \quad (12)$$

It will be shown later that this assumption is valid, since the ratio of the uninhibited to the inhibited rate is independent of pressure.

The rate of reaction (10) is given by I where I is the number of quanta of λ2537 entering the cell per second. If the concentration of mercury vapor in the cell were so low that most of the light was transmitted without absorption, then the rate of (10) would be a function of the mercury pressure. However, the mercury pressure in the present instance is high enough (*ca.* 1.8×10^{-3} mm) to absorb all of the incident light and consequently only secondary radiation will be emitted from the cell. The rate of reaction (11) is equal to $1/\tau\cdot[Hg(^3P_1)]\cdot V$ where τ is the average life of a $Hg(^3P_1)$ atom and V is some arbitrary volume. The rate of (12) is given by $k_{12}\cdot[Hg(^3P_1)]\cdot[C_2H_2]\cdot V$ and since the chain length φ is practically independent of pressure then

$$R_p/\varphi = k_{12}\cdot[Hg(^3P_1)]\cdot[C_2H_2]\cdot V,$$

where R_p is the observed rate of polymerization. Eliminating $[Hg(^3P_1)]$ by the steady-state method, we have

$$\frac{1}{R_p}=\frac{1/\tau}{k_{12}\cdot I}\cdot\frac{1}{\varphi}\cdot\frac{1}{[C_2H_2]}+\frac{1}{\varphi I}.$$

TABLE I. Initial rates *vs.* acetylene concentration.

25°C		300°C	
$[C_2H_2]$ molecules/cc	Rate molecules/sec.	$[C_2H_2]$ molecules/cc	Rate molecules/sec.
5.30×10^{15}	$1.2_8\times10^{15}$	7.3×10^{15}	5.5×10^{15}
8.17	1.5_8	13.4	7.3
10.85	1.7_3	18.7	9.8
13.58	2.4_8	25.8	13.7
19.32	3.0_8	56.5	19.5
28.90	4.9_0	56.5	16.6
40.10	5.3_8	81.2	23.4
68.6	6.3_0		
90.4	5.8_8		
140.2	6.3_7		

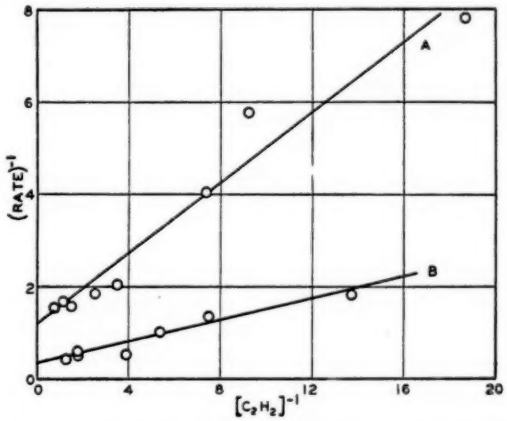


FIG. 2. Reciprocal of the rate in sec. molecules$^{-1}\times10^{16}$ *vs.* reciprocal of the acetylene concentration in cc molecules$^{-1}\times10^{17}$. *A*, 25°C (Series I); *B*, 300°C.

[5] D. J. Le Roy and E. W. R. Steacie, Ind. Eng. Chem. Anal. Ed. (in press).

[6] E. W. R. Steacie and D. J. Le Roy, J. Chem. Phys. **10**, 22 (1942).

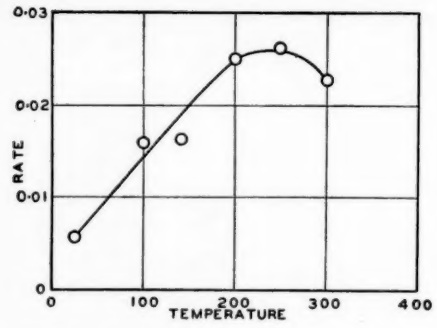


FIG. 3. Rate of pressure decrease in mm per min. *vs.* temperature in °C, for a constant initial acetylene pressure of 9.4×10^{-8} mole per cc.

This is the analog of the Stern-Volmer equation for the quenching of resonance radiation with the exception that the effective value of τ will be somewhat larger than its real value of 10^{-7} sec. due to imprisonment. The validity of the equation can be tested by plotting the reciprocal of the rate against the reciprocal of the acetylene concentration. A straight line should be obtained, with slope $1/(\tau\cdot\varphi\cdot k_{12}\cdot I)$ and with intercept $1/(\varphi\cdot I)$. The ratio of the slope to the intercept is $1/(\tau\cdot k_{12})$ and

$$k_{12}=2(2\pi)^{\frac{1}{2}}\sigma^2\left[\frac{(M_1+M_2)\cdot RT}{M_1\cdot M_2}\right]^{\frac{1}{2}},$$

where σ^2 is the quenching cross section, M_1 and M_2 are the molecular weights of acetylene and mercury, respectively, R is the gas constant in ergs per mole per degree, and T is the absolute temperature.

Data for 25°C (Series I) and 300°C (Series II) are given in Table I, and the reciprocal of the rate is plotted against the reciprocal of the acetylene concentration in Fig. 2. The concentrations and rates for the high temperature have been corrected for the fact that part of the system was at 300°C. The corresponding values of σ^2 are 19.4×10^{-16} cm² and 13.7×10^{-16} cm². In view of the uncertainties in evaluating the initial slopes of the various rate curves and in drawing the best straight line in Fig. 2 (the method of least squares was used) the agreement is fairly satisfactory. Unfortunately, the quenching cross section for this interaction has never been determined by conventional methods but a comparison of the results for Cd($^3P_1$) atoms with acetylene and ethylene[7] and of Hg($^3P_1$) atoms with ethylene[8] would seem to indicate that the results of this somewhat unorthodox method are of the right order of magnitude.

Effect of Temperature on the Rate

A series of runs at a constant acetylene concentration of 9.4×10^{-8} mole per cc was made over the range 25°C to 300°C. The results are given in Fig. 3. The apparent rate increases by a factor of 4 to 4.5 and then appears to flatten off or even decrease. However, the actual temperature coefficient is not necessarily given by Fig. 3 for various reasons, among them the fact that the concentration of mercury vapor is less at 300°C than it is at 25°C. A more important quantity than the apparent temperature coefficient is the temperature coefficient of the chain length. This can be obtained from the quenching curves (Fig. 2). As mentioned above the curve cuts the vertical axis at the point $1/\varphi I$, so we have

$$\varphi_{300}/\varphi_{25}=I_{25}/I_{300}\cdot(\text{intercept})_{25}/(\text{intercept})_{300}.$$

A comparison of the rates at 25°C for Series I and II showed that $I_{25}=1.1\times I_{300}$. (The rate is directly proportional to the light intensity as shown below.) The intercept of the 25° curve is at 1.22×10^{-16} sec. molecule^{-1} and that of the 300° curve 0.364×10^{-16} sec. molecule^{-1}. $\varphi_{300}/\varphi_{25}$ is then approximately 3.7 in close agreement with the results of Fig. 3.

Effect of Light Intensity

By inserting a calibrated screen between the lamp and the cell the light intensity could be

TABLE II. Inhibition by nitric oxide—nitric oxide used up in the reaction. 25°C.

C_2H_2	Percent NO	$-\Delta P_{obs.}$	$-\Delta P_{NO}$
4.6 mm	1.8	0.27 mm	0.06 mm
	3.5	.10	.09
	5.3	.07	.11
	14.3	.07	.08
40.0 mm	1.8	.19	.21
	3.3	.16	.17
	5.5	.12	.09

[7] E. W. R. Steacie and D. J. Le Roy, J. Chem. Phys. 11, 164 (1943).
[8] E. W. R. Steacie, Can. J. Research **B18**, 44 (1940).

reduced to 0.315 times its full value. The corresponding ratio of the rates was 0.35 at 25°C and 0.32 at 75°C, indicating that the rate is directly proportional to the light intensity.

Quantum Yield

The quantum yield of the reaction was measured by Jungers and Taylor.[3] Their value of $\leqslant 6.5$ was based on the quantum yield of hydrogen peroxide formation in the mercury photosensitized hydrogen-oxygen reaction, but since there is considerable disagreement about the correct value of this quantity[9, 10] the quantum yield of the acetylene polymerization was redetermined using uranyl oxalate as the actinometer. The procedure has already been described.[11] A value of 4.5 ± 1.2 was found at 40-mm pressure and 25°C. At this pressure the quenching was found to be practically complete (from absorption measurements) so the number of quenching collisions should be the same as the number of light quanta entering the cell.

Inhibition by Nitric Oxide

On the basis of any excited molecule mechanism one would not expect the polymerization to be inhibited by nitric oxide. That such an inhibition does occur is shown by Fig. 4. The data have been corrected to allow for quenching by nitric oxide. Mitchell and Zemansky[12] give 35.3×10^{-16} cm² as the quenching cross section for $Hg(^3P_1)$ atoms with nitric oxide and since its molecular weight is about the same as that of acetylene it was assumed that nitric oxide was as efficient as acetylene in removing $Hg(^3P_1)$ atoms. However, the quenching in this case is largely of a physical nature since no pressure change was observed in prolonged runs with nitric oxide alone.

To ascertain whether the inhibition might be due to collisional deactivation of excited acetylene molecules, carbon dioxide was substituted for nitric oxide. Although it should be at least as effective as nitric oxide in this respect there was no appreciable decrease in rate with concentrations as high as 50 percent. The small quenching cross section of carbon dioxide (3.54×10^{-16} cm²)[12] prevented it from removing any appreciable fraction of $Hg(^3P_1)$ atoms.

The data in Table II show that some nitric oxide is used up in the reaction. All runs were of 60 minutes' duration with the exception of the fourth, which was 70 minutes. The first column gives the pressure of acetylene, the second the percentage of nitric oxide present, the third the observed pressure decrease in mm, and the fourth the decrease in nitric oxide also expressed in mm. The quantity of nitric oxide used up was determined by condensing the products with liquid air and pumping off and collecting the non-condensible gas by means of a small mercury diffusion pump backed by a Toepler pump. This non-condensible gas was analyzed with the Blacet-Leighton apparatus and identified as nitric oxide.

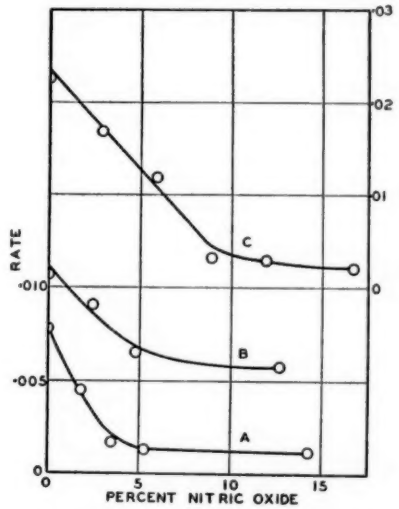


FIG. 4. Rate of pressure decrease in mm per min. *vs.* percent nitric oxide. *A*, 25°C, 4.6 mm C_2H_2 (Series I); *B*, 25°C, 1.75 mm C_2H_2 (Series II); *C*, 300°C, 3.35 mm C_2H_2 (Series III). Left-hand scale for *A* and *B*; right-hand scale for *C*. *B* is shifted vertically on square.

The fact that the polymerization can be inhibited by nitric oxide would seem to indicate that free radicals are involved. The only other alternative would be to assume that inhibition by nitric oxide cannot always be taken as an in-

[9] A. L. Marshall, J. Phys. Chem. **30**, 1078, 1634 (1926); J. Am. Chem. Soc. **45**, 4460 (1932).
[10] W. Frankenburger and H. Klinkhardt, Zeits. f. physik. Chemie **8**, 138 (1930); **15**, 421 (1932).
[11] D. J. Le Roy and E. W. R. Steacie, J. Chem. Phys. **9**, 829 (1941).
[12] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, 1934).

dication of the presence of free radicals. If the polymerization does take place by a free radical process a plausible mechanism would be

$$Hg(^3P_1)+C_2H_2=C_2H+H+Hg(^1S_0), \quad (13a)$$

$$=C_2H+HgH, \quad (13b)$$

$$\text{or}=HgC_2H+H, \quad (13c)$$

followed by

$$C_2H+C_2H_2=C_4H_3, \quad (14)$$

$$H+C_2H_2=C_2H_3, \quad (15)$$

together with similar reactions for the higher radicals. Reaction (13c) is an interesting possibility in view of the fact that mercury is used up in the reaction. In the presence of nitric oxide we would have

$$C_2H+NO=X \quad (16)$$

and

$$H+NO=HNO. \quad (17)$$

If the chain length is not too short the rate of the uninhibited polymerization would be given by

$$R_p=k_p[C_2H_2]\cdot\sum,$$

where k_p is an average rate constant for the various elementary reactions involving the association of acetylene with the free radicals and $\sum$ is the sum of a number of concentration terms related to these radicals. And in the presence of nitric oxide we would have

$$R_i=k_i[NO]\cdot\sum,$$

where R_i is the rate of the inhibition reaction, k_i is an average rate constant for the association of nitric oxide with the various radicals, and $\sum$ has the same meaning as before.

As a first approximation $k_p=A_p\exp(-E_p/RT)$ and $k_i=A_i\exp(-E_i/RT)$ and hence under the experimental condition that $R_p=R_i$ we have

$$A_p\exp(-E_p/RT)[C_2H_2]'=A_i\exp(-E_i/RT)[NO]',$$

where $[C_2H_2]'$ and $[NO]'$ are the concentrations of acetylene and nitric oxide such that the two rates are equal. Neglecting the difference in A as compared to E,

$$E_p-E_i=RT\ln[C_2H_2]'/[NO]'.$$

Initial rates are given as a function of the percentage of nitric oxide in Fig. 4. At half-inhibition the chance of a radical reacting with nitric oxide is equal to the chance of it reacting with acetylene and consequently $R_p=R_i$ when $[C_2H_2]$ and $[NO]$ are such that the over-all rate is halfway between the uninhibited rate and that of the maximally inhibited reaction. As would be expected, more nitric oxide is required for complete inhibition at 300°C than at 25°C. From the ratio $[C_2H_2]'/[NO]'$ the values 2.4, 2.1, and 3.4 kcal. are obtained for E_p-E_i for 25°C (Series I), 25°C (Series II), and 300°C (Series II), respectively. Since the activation energies for the reaction of nitric oxide with radicals are usually considered to be small[13] it is probable that the corresponding values for the chain-propagating reactions are also small. Assuming a value of 3 kcal. for E_p the rate at 300°C would be approximately 11 times that at 25°C. This may be compared to the value of 4.0 obtained from the temperature coefficient of the uninhibited reaction (Fig. 3) and to the value 3.7 obtained for the temperature coefficient of the chain length. All three point to the fact that the polymerization is not very sensitive to temperature.

Inhibition by nitric oxide can also be used to show the effect of pressure on the chain length. Experiments at 25°C showed that the ratio of the rates of the uninhibited to completely inhibited reaction was the same at 4.6-mm as at 40-mm acetylene pressure within the accuracy of the rate measurements. This would indicate that the chain length is independent of pressure.

Products of the Reaction

Further evidence against an excited molecule mechanism for the polymerization would be the production of gaseous products. Kemula and Mrazek[14] found small amounts of ethylene and ethane as well as benzene in the photochemical polymerization of acetylene and Lind and Livingston[15] took the production of the first two as evidence for a free radical mechanism. Although a more elaborate analysis of the products will be deferred to a later publication, there is

[13] J. S. A. Forsyth [Trans. Faraday Soc. **37**, 312 (1941)] found a value of 6.5 kcal. for the activation energy of the reaction of methyl radicals with nitric oxide. However, there is reason to believe that the value would be much smaller in the case of highly unsaturated radicals.

[14] W. Kemula and St. Mrazek, Zeits. f. physik. Chemie **B23**, 358 (1933).

[15] S. C. Lind and R. Livingston, J. Am. Chem. Soc. **56**, 1550 (1934).

TABLE III. Inhibition of the cadmium photosensitized polymerization.

Wave-length	Rate in absence of NO / Rate with 20 percent NO
3261A – Cd($^3P_1$)	2.1±0.5
2288A – Cd($^1P_1$)	3.0±1

evidence that some product or products with a carbon number of two and a small amount of hydrogen are formed. That this observation was not made by previous investigators is probably due to the fact that the total volume of these products is equivalent to only about one-fifth of the amount of acetylene used up.

B. The Cadmium Photosensitized Reactions

A few runs were made to investigate the Cd($^3P_1$) and Cd($^1P_1$) photosensitized polymerization. Inhibition by nitric oxide occurred in both cases. Some difficulty was encountered due to the fact that nitric oxide reacted rapidly with cadmium oxide and there was usually a slight trace of this present. There is also a possibility that it reacts slowly with cadmium itself. These sources of error were largely overcome by using a freshly cleaned cell for each run and the minimum amount of cadmium. The extent of inhibition increased with the amount of nitric oxide so the final runs were made with 20 percent nitric oxide—sufficient to produce maximum inhibition. No correction was made to allow for quenching by nitric oxide but the error would not be significant. Table III gives the average inhibition with 2.3 mm of acetylene and 20 percent nitric oxide. The results are only approximate but definitely show inhibition in both cases with possibly a slightly larger value at the shorter wave-length.

Discussion

Burnham and Pease[16] have recently shown that the thermal polymerization of acetylene is inhibited by nitric oxide and have suggested that free radicals are involved. If we are to accept the usual interpretation of the effect of nitric oxide on a reaction a similar conclusion would have to be drawn from the present experiments. If the reaction proceeded by an excited molecule mechanism it would have to be assumed that nitric oxide can react with acetylene molecules excited by collision with Hg($^3P_1$) atoms although it has been shown that this is not the case with excited ethylene.[1] It has also been shown that there is no thermal reaction between nitric oxide and acetylene under the conditions obtaining in the present experiments.[17]

If the reaction does involve free radicals it is difficult to see how the primary step could be other than

$$Hg(^3P_1)+C_2H_2=C_2H+H+Hg(^1S_0), \quad (13a)$$

$$=C_2H+HgH \quad (13b)$$

$$\text{or } =HgC_2H+H. \quad (13c)$$

This reaction is the analog of (5) and would be possible only if the C–H bond strength in acetylene is less than 112.2 kcal. (or 120.7 if HgH is formed). Since reaction (5) does take place to a small extent with ethylene it would appear that its C–H bond strength falls within the upper limit. Stevenson[18] has estimated from electron impact data that the C–H bond strength in ethylene is 91.1 kcal., well within the upper limit set by our experiments, so it is not improbable that the value for acetylene is low enough to permit reaction (13) to take place.

Additional evidence bearing on, but not necessarily confirming, a low value for the C–H bond strength in acetylene is the work of Geib and Steacie[19] on the reaction of deuterium atoms with acetylene. They found an activation energy of <5 kcal. for the deuterization and suggested two

[16] H. D. Burnham and R. N. Pease, J. Am. Chem. Soc. 64, 1404 (1942).

[17] It has been suggested by the reviewer that the absence of "feedback" might indicate that there is some reaction between nitric oxide and excited acetylene, perhaps under the influence of mercury. However, transitory inhibition by nitric oxide is by no means general and even in the one case [L. S. Echols and R. N. Pease, J. Am. Chem. Soc. 61, 1024 (1939)] where it has been ascribed to feedback the evidence for an equilibrium of the type R+NO⇌RNO is not firmly established. In any case if such an equilibrium did exist it would probably be shifted much farther to the right in the present range of temperature than in the case of the butane decomposition.

[18] D. P. Stevenson, J. Am. Chem. Soc. 65, 209 (1943).

[19] K. H. Geib and E. W. R. Steacie, Zeits. f. physik. Chemie B29, 215 (1935).

possible mechanisms,

I and II

$$D+C_2H_2 = C_2H_2D$$
$$D+C_2H_2D = C_2HD+HD$$
$$D+C_2H_2 = C_2H+HD$$
$$D+C_2H = C_2HD.$$

If the observed activation energy corresponds to that of the primary step of mechanism II, then the C−H bond strength in acetylene must be <108 kcal. However, there is, at present, no method of deciding between mechanisms I and II.

A free radical process for the polymerization of acetylene by $Cd(^3P_1)$ atoms is not precluded in spite of its low energy (87.3 kcal.), since CdH formation would increase the available energy by 15.5 kcal. and CdC_2H formation would probably also increase it. Certainly the inhibition of both the $Cd(^3P_1)$ and $Cd(^1P_1)$ reactions by nitric oxide suggests that at least part of the reaction proceeds by a free radical process.

If the photosensitized polymerization does not involve free radicals the experimental facts could be explained by Melville's mechanism [reactions (6)–(9)] together with chain-stopping reactions of the type

$$C_2H_2^* + NO = C_2H_2NO. \qquad (14)$$

CONCLUSION

The major feature of the present investigation is the inhibition by nitric oxide. The interpretation of the results as evidence for a free radical mechanism is based on the following considerations: (a) Nitric oxide can inhibit reactions in which free radicals are known to be involved; (b) it will not inhibit certain reactions which are believed not to involve free radicals; (c) it does not react with excited ethylene molecules; (d) there is some evidence that sufficient energy is available to break the C−H bond in acetylene even with $Cd(^3P_1)$ atoms; (e) gaseous products including hydrogen are formed; (f) although other workers have postulated an excited molecule mechanism, none of their data is inconsistent with a free radical mechanism.

On the basis of this evidence it seems probable that the mercury photosensitized polymerization of acetylene proceeds, at least partially, by a free radical process. It should be pointed out, however, that it is not impossible to explain the results on the basis of an excited molecule mechanism. It is hoped that future work will make it possible to decide the question and to establish a mechanism in detail.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 4 APRIL, 1944

Theory of Molecular Size Distribution and Gel Formation in Branched Polymers

II. General Cross Linking *

WALTER H. STOCKMAYER†
Department of Chemistry, Columbia University, New York, New York

(Received January 14, 1944)

A statistical calculation of the gel point and of the molecular size distribution is made for cross-linked high polymers of arbitrary initial size distribution. The weight-average polymerization degree of the cross-linked polymer depends only on the weight-average polymerization degree of the initial polymer and the degree of cross linking. The results obtained also apply to certain vinyl-divinyl copolymers. Polymerization degrees can be estimated from observations of the gel point.

1. INTRODUCTION

IT is well known and practically important that, when sufficiently frequent branching or cross linking of chains occurs during the course of a polymerization or polycondensation reaction, the enhanced capacity for further growth of the larger molecules (due to their larger number of unreacted end groups) leads ultimately to the formation of a few network structures so huge that the material changes rather abruptly from a fluid to a gel. The statistical theory of such reactions, developed by Flory[1–4] and embellished by the writer,[5] has had conspicuous success in predicting the gel point[1] for the several polycondensations to which it has been applied. In this paper the theory is extended to a more general case than those previously considered; namely, the cross linking of a system of chains with *arbitrary* initial size distribution. The rather formidable size distribution equations which are obtained lead to relatively simple expressions for the gel point and the several average polymerization degrees. It transpires that these equations should also apply to some vinyl-divinyl copolymers, if certain plausible assumptions are made.

2. THE GEL POINT

The polymeric molecules of various sizes which initially comprise the system will be called *chains*, although they need not necessarily be linear. In the simplest case, each monomer unit in a chain bears one functional group which can be linked through chemical reaction to others of its kind, either with or without the aid of an added cross-linking agent.[6] All functional groups are assumed to be similar and of the same reactivity. The term *molecule* will be reserved for the aggregates which exist after some cross linking has taken place; a molecule therefore consists of one or more chains. Let the system contain N_1 monomeric chains, N_2 dimeric chains, ———, N_s s-meric chains, — etc. The number-average size (polymerization degree) of the chains is thus

$$\lambda_n = \sum sN_s / \sum N_s, \tag{1}$$

and the weight-average size is

$$\lambda_w = \sum s^2 N_s / \sum sN_s = \sum sw_s, \tag{2}$$

where w_s, the weight fraction of s-meric chains, is given by

$$w_s = sN_s / \sum sN_s. \tag{3}$$

Since each monomeric unit bears one functional group, w_s is also the fraction of groups residing on s-meric chains.

It will be assumed (as in the previous papers[1–5]) that when cross linking occurs no rings can form; that is, any two chains can be cross linked to

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research at Columbia University.

† Present address: Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[1] P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).
[2] P. J. Flory, J. Am. Chem. Soc. **63**, 3091 (1941).
[3] P. J. Flory, J. Am. Chem. Soc. **63**, 3096 (1941).
[4] P. J. Flory, J. Phys. Chem. **46**, 132 (1942).
[5] W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943), hereinafter called I.

[6] Vulcanization processes are obviously of this type. For several other examples, see B. S. Garvey, Jr., C. H. Alexander, F. E. Küng, and D. E. Henderson, Ind. Eng. Chem. **33**, 1060 (1941).

each other at only one point. This assumption introduces only a moderate error in undiluted systems, at least up to the gel point. Then when a fraction α of the functional groups in the system has become involved in cross links, the number of molecules M is equal to the number of chains less the number of linkages, or

$$M=\sum N_s-(\alpha/2)\sum sN_s \\ =\sum N_s(1-\alpha\lambda_n/2). \quad (4)$$

The quantity $\gamma\equiv\alpha\lambda_n$ is the (number) average number of cross-linked units per chain, and was called by Flory[3] the *cross-linking index*.

A simple procedure[1] suffices for the prediction of the gel point. Consider a particular cross-linked group attached to some chain chosen at random from the system. The probability that the reacted group at the other end of the cross link is on an s-meric chain is w_s. Since this second chain carries s groups in all, and since the probability that a group has formed a cross link is α, the expected number of *additional* chains to which this second chain is connected is $\alpha(s-1)$. Therefore the average expectance of additional chains ν (averaged over all possible chain sizes) is

$$\nu=\sum_s w_s\alpha(s-1)=\alpha(\lambda_w-1). \quad (5)$$

If ν exceeds unity, there is a finite probability that a chain chosen at random from the system belongs to an "infinitely large" molecule.[1] Hence the critical value of α for the appearance of such large molecules, physically identified with the gel point, is

$$\alpha_c=(\lambda_w-1)^{-1}. \quad (6)$$

If the initial material is a fairly high polymer, so that $\lambda_w\gg1$, the critical value of the cross-linking index is

$$\gamma_c\equiv\alpha_c\lambda_n\simeq\lambda_n/\lambda_w. \quad (7)$$

If all chains are of equal length, $\lambda_n=\lambda_w$ and $\gamma_c=1$, as previously found by Flory.[3] The great heterogeneity of the molecular size distribution at the gel point is illustrated by the value of the number-average number of chains per molecule, which equals

$$\sum N_s/M=(1-\gamma/2)^{-1}, \quad (8)$$

from Eq. (4). For most synthetic linear polymers, λ_w/λ_n lies between 1.5 and 2, so that when such substances are cross linked $\sum N_s/M$ is only about 4/3 to 3/2 at the gel point, although some extremely large molecules are present.

We wish also to consider the case of a copolymer, in which only a fraction ρ of the monomeric units contained in the chains bears functional groups susceptible to the cross-linking reaction. If N_{sl} represents the number of s-meric chains carrying l reactive groups each, the fraction of the reactive groups borne by chains carrying l such groups each is

$$f_l=\sum_s lN_{sl}/\sum_s\sum_l lN_{sl}, \quad (s\geq l\geq1). \quad (9)$$

Repeating the previous argument, we now find the average expectance of additional chains to be

$$\nu=\sum_l f_l\alpha(l-1) \\ =\alpha\sum_s\sum_l l(l-1)N_{sl}/\sum_s\sum_l lN_{sl}. \quad (10)$$

The general evaluation of this expression demands an explicit formula for N_{sl}. If the reactive units are distributed *at random* throughout all the chains ("true copolymer"),[7] we may write

$$N_{sl}=N_s\binom{s}{l}\rho^l(1-\rho)^{s-l}, \quad (11)$$

where N_s is the total number of s-meric chains of all compositions. In this case the sums are easily found, with the result

$$\nu=\alpha\rho(\lambda_w-1), \quad (12)$$

so that the gel point is now given by

$$\alpha_c=[\rho(\lambda_w-1)]^{-1}, \quad (13)$$

as reported in a recent note.[8] Since the cross-linking index is now given by $\gamma=\alpha\rho\lambda_n$, its critical value is still (for long chains) equal to λ_n/λ_w as expressed in Eq. (7).

For other than random copolymers, Eqs. (12) and (13) will in general not be correct. They may be formally retained by altering the significance of ρ to that of an unknown parameter which approaches the actual average composition of the chains in the case of a true copolymer. In general, this redefined ρ may vary with the extent of polymerization as well as with the average composition. It appears, however, that in some cases

[7] F. T. Wall, J. Am. Chem. Soc. **63**, 1862 (1941).
[8] W. H. Stockmayer and H. Jacobson, J. Chem. Phys. **11**, 393 (1943).

such variation can be rather small.[9] It is probably safe to expect that ρ will be approximated fairly well by the average composition if the chains have been formed by a single batch copolymerization. If, however, the chains are mechanical mixtures of rather different copolymers, such an approximation will be poor.

It has already been pointed out[8] that in cases where Eq. (13) holds it is possible in principle to determine λ_w experimentally by observations of the gel point. Thus the weight-average polymerization degree of polyvinyl acetate, for example, could be obtained by measuring the extent of its ester interchange with diethyl phthalate at gelation.[6]

3. MOLECULAR SIZE DISTRIBUTION

In this section the methods developed in I[5] are employed to derive the actual distribution of molecular sizes up to the gel point. To avoid excessively cumbersome equations, the detailed treatment is restricted to the case that all units in the chains carry a reactive group ($\rho=1$).

The description of any single molecule requires specification of the number of chains of each size which it contains. We denote by n_1, n_2, n_3, $\cdots n_s$, etc., these numbers of chains, and for brevity represent any particular set of these numbers by the symbol $\{n_s\}$. The symbol $m\{n_s\}$ will be used for the number of molecules described by a particular set $\{n_s\}$. The most probable molecular size distribution is then written (cf. I)

$$m\{n_s\}=A\omega\{n_s\}\prod_s(\xi_s^{n_s}/n_s!), \tag{14}$$

where A and all the ξ_s are Lagrangian multipliers to be evaluated subsequently, and $\omega\{n_s\}$ is the number of different ways in which a molecule described by $\{n_s\}$ can be constructed from its constituent chains. Generalization of the argument of I (Appendix A) gives the result

$$\omega\{n_s\}=\frac{(\sum sn_s-\sum n_s)!}{(\sum sn_s-2\sum n_s+2)!}\prod_s s^{n_s}. \tag{15}$$

Now the Lagrangian multipliers must be so chosen that

$$M=\sum_{\text{all }\{n_s\}} m\{n_s\}, \tag{16}$$

and

$$N_t=\sum_{\text{all }\{n_s\}} n_t m\{n_s\}, \text{ for all } t. \tag{17}$$

The sums go over all possible sets $\{n_s\}$, and M is given by Eq. (4). In the simpler cases treated in I, the prototypes of Eqs. (16) and (17) required summations which were relatively easy to perform directly; here an heuristic attack is of advantage. Experience with the simpler cases suggests the substitutions

$$s\xi_s=w_s\alpha(1-\alpha)^{s-2}, \tag{18}$$

$$A=(\sum sN_s)(1-\alpha)^2/\alpha. \tag{19}$$

It is shown in the Appendix that this choice does satisfy Eqs. (16) and (17). The distribution law, obtained by substituting Eqs. (15), (18), and (19) into Eq. (14), is thus

$$m\{n_s\}=(\sum sN_s)\frac{(\sum sn_s-\sum n_s)!}{(\sum sn_s-2\sum n_s+2)!}\alpha^{\sum n_s-1}$$
$$\times(1-\alpha)^{\sum sn_s-2\sum n_s+2}\prod_s(w_s^{n_s}/n_s!). \tag{20}$$

This law may be employed to derive the weight-average molecular size $\bar{P}_w$ of the cross-linked polymer. A molecule contains $\sum sn_s$ units in all, so that the weight fraction of molecules described by $\{n_s\}$ is simply

$$W\{n_s\}=(\sum sn_s)m\{n_s\}/(\sum sN_s). \tag{21}$$

Then the weight-average molecular size is

$$\bar{P}_w=\sum_{\text{all }\{n_s\}}(\sum sn_s)W\{n_s\}. \tag{22}$$

As shown in the Appendix, carrying out the summation yields the result

$$\bar{P}_w=\lambda_w(1+\alpha)/[1-\alpha(\lambda_w-1)]. \tag{23}$$

Since this equation requires $\bar{P}_w$ to become infinite at $\alpha_c=(\lambda_w-1)^{-1}$, indicating the presence of some very large molecules, Eq. (23) may be regarded as furnishing an independent derivation of Eq. (6).

It is apparent that in the special case that all chains have the same size s, Eq. (20) reduces to

$$m_n=sN\alpha^{n-1}(1-\alpha)^{sn-2n+2}\frac{(sn-n)!}{n!(sn-2n+2)!}, \tag{24}$$

which was derived in I. If, in addition, $s\gg1$, use

[9] C. S. Marvel and G. L. Schertz, J. Am. Chem. Soc. **65**, 2054 (1943).

of the Stirling formula leads to the following expression for the weight fractions:

$$W_n = n^{n-1}(\gamma e^{-\gamma})^n/n!\gamma, \qquad (25)$$

where γ, equal to $s\alpha$, is the cross-linking index. The above equation was derived by Flory[3] by methods appropriate to this special case.

The molecular size distribution for the case $\rho<1$ (cf. Section 2) could in principle be found by straightforward extension of the methods described above. It is sufficient to remark here that for a "true copolymer" the formulae for the average molecular sizes carry over if α is replaced everywhere by $\alpha\rho$. If the chains are long, the average sizes are given by the simple expressions

$$\bar{P}_n = \lambda_n/(1-\gamma/2), \qquad (26)$$

$$\bar{P}_w = \lambda_w/(1-\gamma/\gamma_c), \qquad (27)$$

with $\gamma=\alpha\rho\lambda_n$ and $\gamma_c=\lambda_n/\lambda_w$. Formally these equations may be retained for other than random copolymers by substitution of an appropriate parameter in place of ρ, but as stated previously, such maneuvers require considerable understanding of the copolymerization reaction.

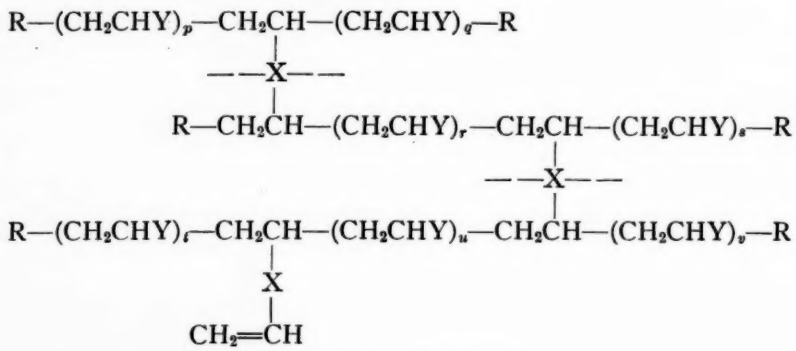
The foregoing results are unfortunately of little aid in characterizing materials for which the cross-linking reaction has progressed beyond the gel point. Here the inclusion of ring formation is essential. The treatment employed by Flory[3] (which is probably a fair approximation) shows in any case that the residual fraction of relatively small molecules (the extractable "sol fraction") becomes negligible if the reaction proceeds much beyond the gel point. For interpreting the physical properties (such as rubber-like elasticity) of these materials the "number of molecules" has little significance; what is required is the number and size distribution of the chain portions lying between cross links.[10,11]

4. VINYL-DIVINYL COPOLYMERS

The copolymerization of a vinyl derivative with sufficient quantity of a divinyl derivative also leads to gelled three-dimensional polymers,[6,12,13] but the mechanism differs from the cases we have treated above, in that polymerization and cross linking are concomitant rather than consecutive. It nevertheless appears that under certain conditions, which we shall discuss, the results just obtained may be applied to these systems.[8]

Some of the assumptions required are quite generally obeyed.[14] One of these is that at any instant the fraction of material involved in active growing chains is negligible compared to the amounts of stable polymer and residual monomer.

The stable polymer consists of *molecules*, which are subdivided for our purpose into *chains*. These chains may be most easily pictured as the aggregates which would remain if suddenly every doubly-reacted divinyl unit in the polymer were to be cut in half. If $CH_2=CHY$ and $CH_2=CH-X-CH=CH_2$ represent the two monomers, the molecule pictured below would consist of three chains.



[10] H. M. James and E. Guth, J. Chem. Phys. 11, 455 (1943).
[11] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. 11, 512 (1943).
[12] H. Staudinger and W. Heuer, Ber. 68, 1618 (1935).
[13] R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. A163, 205 (1937).
[14] For recent concepts of the mechanism of addition polymerization, consult: J. Abere, G. Goldfinger, H. Mark, and H. Naidus, Ann. N. Y. Acad. Sci. 44, 267 (1943); C. C. Price, *ibid.* 44, 351 (1943); H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, *ibid.* 44, 371 (1943).

In this example, R represents fragments from a peroxide type catalyst,[14] and the cutting process described above would occur at the places indicated by dashed lines. With the above definition of a chain, it is not necessary to make special provision for any branching[15] which might result from chain-transfer processes, and which seems to occur to a small but noticeable extent in the polymerization of monovinyl derivatives. If such branching takes place, the "chains" will not all be topologically linear, but this fact in no way alters the statistical problem.

It is clear that, if all the double bonds located on divinyl units have the same probability of reaction α, then Eqs. (9) and (10) can be applied to the case at hand. Here N_{sl} is the number of stable polymer chains, consisting of s reacted double bonds in all, which contain l reacted double bonds attached to divinyl units. In order that α be an independent probability, the rates of all steps in the polymerization mechanism must be independent of the size of the molecules to which the reacting groups adhere. It has been demonstrated experimentally[16] that this situation obtains in polyesterification reactions. With regard to vinyl polymerization, Norrish and Smith[17] have suggested that the termination rate (which may be diffusion-controlled) decreases with an increase in chain length, at least for methyl methacrylate. It is difficult, however, to understand such a variation physically, in view of the well-known segment-flow behavior of flexible long chains.[18] An alternative explanation of the effects observed by Norrish and Smith is not improbable, and is to be preferred in the absence of further evidence. Herington and Robertson,[19] for example, find that the molecular size distribution of polystyrene[20] is in satisfactory accord with the assumption that the variation of reactivity with molecular size is insignificant.

With this assumption of equal reactivity, α becomes the reacted fraction of the double bonds attached to divinyl units, and could be found experimentally from the composition of the copolymer and the over-all reacted fraction of double bonds. The problem of evaluating the sums of Eq. (10) in the general case has already been discussed. In the special case of a "true copolymer," Eq. (13), and the distribution laws of Section 3, may be employed, with ρ equal to the composition of the original system (expressed as the over-all fraction of double bonds residing on divinyl units) and α equal to the over-all reacted fraction of double bonds. It should be noted that α is not identical with the weight fraction of polymer formed, since the polymer contains some unreacted double bonds (on divinyl units of which only one bond has reacted). The quantity λ_w is equal to the weight average number of (reacted) double bonds per chain.[21]

The ideal case just discussed might be realizable experimentally if the two monomers were judiciously chosen. An especially interesting situation would occur if the rates were independent of the composition ρ, for then λ_w in the copolymer would equal the weight average polymerization degree of a polymer prepared from the pure monovinyl reactant ($\rho=0$) under identical conditions.[8]

Apparently no suitable experimental data on the gel point in vinyl-divinyl copolymerizations have yet been published.[22] The well-known case of styrene and *p*-divinylbenzene[12] is not described by Eq. (13), since the latter substance enters the polymer more readily than styrene. Qualitatively the agreement is satisfactory. If temperature and concentrations are such that λ_w is 2000, then 0.05 equivalent percent (about 0.03 weight percent) of divinyl-benzene is sufficient to produce an infusible polymer according to Eq. (13); the actual limit would be expected to be even lower.

The writer is grateful to Homer Jacobson for helpful discussion and criticism.

[15] G. V. Schulz, Zeits. f. physik. Chemie **B44**, 227 (1939).
[16] P. J. Flory, J. Am. Chem. Soc. **61**, 3334 (1939).
[17] R. G. W. Norrish and R. R. Smith, Nature **150**, 336 (1942).
[18] W. Kauzmann and H. Eyring, J. Am. Chem. Soc. **62**, 3113 (1940).
[19] E. F. G. Herington and A. Robertson, Trans. Faraday Soc. **38**, 490 (1942).
[20] G. V. Schulz, A. Dinglinger, and E. Husemann, Zeits. f. physik. Chemie **B43**, 385 (1939).

[21] If the termination process is a disproportionation of two radicals which leaves a double bond in one chain, or if a solvent takes part in chain transfer, slight modifications are required. At all significant degrees of polymerization, however, these effects are negligible.
[22] Experiments are now in progress in this laboratory.

APPENDIX

First it is to be shown that the distribution law

$$m\{n_s\} = (\sum sN_s)\alpha^{\sum n_s - 1}(1-\alpha)^{\sum s n_s - 2\sum n_s + 2}\frac{(\sum s n_s - \sum n_s)!}{(\sum s n_s - 2\sum n_s + 2)!}\prod_s \frac{w_s^{n_s}}{n_s!} \tag{A1}$$

satisfies the conditions

$$M = \sum_{\text{all } \{n_s\}} m\{n_s\} = (\sum N_s)(1 - \alpha\lambda_n/2), \tag{A2}$$

and

$$N_t = \sum_{\text{all } \{n_s\}} n_t m\{n_s\} \text{ (for all } t). \tag{A3}$$

Expanding the power of (1-α) in Eq. (A1), we have

$$M = (\sum sN_s)\sum_{\text{all } \{n_s\}}\sum_k (-1)^k \alpha^{\sum n_s + k - 1}\frac{(\sum s n_s - \sum n_s)!}{k!(\sum s n_s - 2\sum n_s + 2 - k)!}\prod_n \frac{w_s^{n_s}}{n_s!}. \tag{A4}$$

By putting $\sum n_s + k = q$ and eliminating k, this may be written

$$M = (\sum sN_s)\sum_{q=1}^{\infty}\frac{(-\alpha)^q}{q!}\sum_{\sum n_s \le q}\prod_s \frac{(-1)^{\sum n_s} q!(\sum s n_s - \sum n_s)!\, w_s^{n_s}}{n_s!(q - \sum n_s)!(\sum s n_s - \sum n_s + 2 - q)!}, \tag{A5}$$

where the second sum is taken over all sets $\{n_s\}$ satisfying the condition $\sum n_s \leqslant q$. Consider now the function

$$F(x) = (1 - \sum w_s x^{s-1})^q = \sum_{\sum n_s \le q}\prod_s \frac{(-1)^{\sum n_s} q!\, w_s^{n_s} x^{\sum s n_s - \sum n_s}}{n_s!(q - \sum n_s)!}, \tag{A6}$$

where q is an integer greater than two. Repeated differentiation gives

$$\left[\left(\frac{d}{dx}\right)^{q-2} F(x)\right]_{x=1} = \sum_{\sum n_s \le q}\prod_s \frac{(-1)^{\sum n_s} q!(\sum s n_s - \sum n_s)!\, w_s^{n_s}}{n_s!(q - \sum n_s)!(\sum s n_s - \sum n_s - q + 2)!}, \tag{A7}$$

which is recognized as a sum required in Eq. (A5). But since this derivative necessarily contains the factor $(1 - \sum w_s)$, its value is zero, and the sum of Eq. (A5) reduces to the terms in $q=1$ and $q=2$. Evaluating these, we obtain

$$M = (\sum sN_s)(\sum w_s/s - \alpha/2) = (\sum N_s)(1 - \alpha\lambda_n/2), \tag{A8}$$

where we have used $\sum w_s/s = \sum N_s/\sum sN_s = 1/\lambda_n$. This proves (A2).

We must now evaluate

$$\sum_{\text{all } \{n_s\}} n_t m\{n_s\} = (\sum sN_s)\sum_{\text{all } \{n_s\}} \alpha^{\sum n_s - 1}(1-\alpha)^{\sum s n_s - 2\sum n_s + 2}\frac{(\sum s n_s - \sum n_s)!}{(\sum s n_s - 2\sum n_s + 2)!}\frac{w_t^{n_t}}{(n_t - 1)!}\prod_s{}' w_s^{n_s}/n_s!, \tag{A9}$$

where the prime on the product sign indicates that the term in t is omitted. If we now put $\nu_t = n_t - 1$, and $\nu_s = n_s$, this becomes

$$\sum_{\text{all } \{n_s\}} n_t m\{n_s\} = w_t(\sum sN_s)\sum_{\text{all } \{\nu_s\}} \alpha^{\sum \nu_s}(1-\alpha)^{\sum s\nu_s - 2\sum \nu_s + t}\frac{(\sum s\nu_s - \sum \nu_s + t - 1)!}{(\sum s\nu_s - 2\sum \nu_s + t)!}\prod_s \frac{w_s^{\nu_s}}{\nu_s!}. \tag{A10}$$

As before, we expand the power of $(1-\alpha)$ and obtain

$$\sum_{\text{all } \{n_s\}} n_t m\{n_s\} = w_t(\sum sN_s)\sum_{q=0}^{\infty}\frac{(-\alpha)^q}{q!}\sum_{\sum \nu_s \le q}\prod_s \frac{(-1)^{\nu_s}(\sum s\nu_s - \sum \nu_s + t - 1)!\, q!\, w_s^{\nu_s}}{(\sum s\nu_s - \sum \nu_s + t - q)!(q - \sum \nu_s)!\, \nu_s!}. \tag{A11}$$

The $(q-1)$st derivative of the function

$$G(x)=x^{t-1}(1-\sum w_s x^{s-1})^q, \quad (q>1), \tag{A12}$$

vanishes for $x=1$ and shows that only the terms in $q=0$ and $q=1$ of Eq. (A11) contribute to the sum. Evaluating these, we find

$$\sum_{\text{all }\{n_s\}} n_t m\{n_s\}=w_t(\sum sN_s)/t=N_t. \tag{A13}$$

Thus the assumed distribution law has been shown to satisfy all necessary conditions.

We now turn to a calculation of the weight average molecular size, which from Eqs. (21) and (22) of the text may be written as

$$\begin{aligned}\bar{P}_w&=\sum_{\text{all }\{n_s\}}(\sum sn_s)^2 m\{n_s\}/(\sum sN_s)\\&=[\sum_t (t^2\sum_{\text{all }\{n_s\}} n_t^2 m\{n_s\})+2\sum_t\sum_{r>t}(rt\sum_{\text{all }\{n_s\}} n_r n_t m\{n_s\})]/(\sum sN_s).\end{aligned} \tag{A14}$$

The procedure resembles that used above. Putting $\nu_t=n_t-2$ and $\nu_s=n_s$, we find

$$\begin{aligned}\sum_{\text{all }\{n_s\}} n_t(n_t-1)m\{n_s\}/(\sum sN_s)&=w_t^2\sum_{\text{all }\{\nu_s\}}\alpha^{\sum\nu_s+1}(1-\alpha)^{\sum s\nu_s-2\sum\nu_s+2t-2}\frac{(\sum s\nu_s-\sum\nu_s+2t-2)!}{(\sum s\nu_s-2\sum\nu_s+2t-2)!}\prod_s\frac{w_s^{\nu_s}}{\nu_s!}\\&=w_t^2\alpha\sum_{q=0}^{\infty}\frac{(-\alpha)^q}{q!}\sum_{\sum\nu_s\le q}\prod_s\frac{(-1)^{\sum\nu_s}(\sum s\nu_s-\sum\nu_s+2t-2)!\,q!\,w_s^{\nu_s}}{(\sum s\nu_s-\sum\nu_s+2t-2-q)!(q-\sum\nu_s)!\,\nu_s!}.\end{aligned} \tag{A15}$$

Now define

$$H(x)=x^{2t-2}(1-\sum w_s x^{s-1})^q. \tag{A16}$$

Expanding multinomially and differentiating q times, we have

$$\left[\left(\frac{d}{dx}\right)^q H(x)\right]_{x=1}=\sum_{\sum\nu_s\le q}\prod_s\frac{(-1)^{\sum\nu_s}(\sum s\nu_s-\sum\nu_s+2t-2)!\,q!\,w_s^{\nu_s}}{(\sum s\nu_s-\sum\nu_s+2t-2-q)!(q-\sum\nu_s)!\,\nu_s!}. \tag{A17}$$

A direct evaluation of this quantity from Eq. (A16) gives

$$\left[\left(\frac{d}{dx}\right)^q H(x)\right]_{x=1}=q![-\sum(s-1)w_s]^q=q!(-1)^q(\lambda_w-1)^q. \tag{A18}$$

Thus, substituting in Eq. (A15) we find

$$\sum_{\text{all }\{n_s\}} n_t(n_t-1)m\{n_s\}/(\sum sN_s)=w_t^2\alpha\sum_{q=0}^{\infty}\alpha^q(\lambda_w-1)^q=w_t^2\alpha/[1-\alpha(\lambda_w-1)]. \tag{A19}$$

Therefore

$$\sum_{\text{all }\{n_s\}} n_t^2 m\{n_s\}/(\sum sN_s)=w_t^2\alpha/[1-\alpha(\lambda_w-1)]+w_t/t, \tag{A20}$$

where we have made use of (A13).

The second sum in Eq. (A14) may be found by a similar procedure, the appropriate auxiliary function being $I(x)=x^{r+t-2}(1-\sum w_s x^{s-1})^q$. The result is

$$\sum_{\text{all }\{n_s\}} n_r n_t m\{n_s\}/(\sum sN_s)=w_r w_t\alpha/[1-\alpha(\lambda_w-1)]. \tag{A21}$$

Substituting Eqs. (A20) and (A21) into Eq. (A14), we get

$$\begin{aligned}\bar{P}_w&=[\sum_t t^2 w_t^2+2\sum_t\sum_{r>t} rtw_r w_t]\alpha/[1-\alpha(\lambda_w-1)]+\sum_t tw_t=\alpha\lambda_w^2/[1-\alpha(\lambda_w-1)]+\lambda_w\\&=\lambda_w(1+\alpha)/[1-\alpha(\lambda_w-1)],\end{aligned} \tag{A22}$$

which is the result given in Eq. (23) of the text.

Cyclotron Targets: Preparation and Radiochemical Separation. II. Krypton

SANBORN C. BROWN,* JOHN W. IRVINE, JR.,† AND M. STANLEY LIVINGSTON*
Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received January 19, 1944)

Radioactive krypton ($T=34h$, e^+, γ) has become a very useful gas for tracer experiments. This isotope can be made by $Br^{79,81}(d, 2n)Kr^{79,81}$. Preparation and separation of this gas have been a routine matter in this laboratory for some time and a brief description of the methods used is of interest. Two different methods will be described. Both are equally good as far as the separation of the krypton is concerned. One method involves very simple manipulation, but requires an apparatus made of monel metal, fused quartz, and Pyrex glass; the other uses only readily obtainable and inexpensive apparatus, but slightly more complicated manipulation.

FUSION METHOD

SODIUM bromide was chosen for bombardment because of its high bromine content and relatively small tendency to be hygroscopic.

The Target

U.S.P. grade NaBr is used as the target material, and the amount used is of the order of 40 grams. The crystals are spread in a thin layer ($\frac{1}{16}$ inch thick) over the surface of a water-cooled copper target plate, which has the surface scored by parallel grooves similar to a coarse file to hold the powder in place. This target plate fits into a cylindrical target chamber.

The target chamber is mounted at the end of a divergent spout attached to the cyclotron[1] through which the emergent beam passes. Between the spout and the target chamber is a dural foil vacuum window to transmit the beam. The energy loss in the 0.001-inch foil is approximately 0.5 Mev and the average distance traversed in the helium before striking the target reduces the energy by another 0.1 to 0.2 Mev. Thus the effective energy of the 14.0-Mev deuteron beam (measured) is about 13.3 Mev.

The target chamber is evacuated and then filled to near atmospheric pressure with helium gas during the bombardment. The helium serves as a cooling agent for the target. The emergent deuteron beam has dimensions of approximately 6 inches by $\frac{3}{4}$ inch high at the location of the target chamber. The target plate is 6 by $5\frac{1}{2}$ inches and is arranged so that it can be tilted into a nearly horizontal position, so the $\frac{3}{4}$-inch beam is spread over the $5\frac{1}{2}$-inch width.

Separation of the Target

After the NaBr has been bombarded, it contains three main radioactive elements: sodium, bromine, and krypton.[2] The radioactive bromine and krypton are to be found as gases trapped in the crystal lattice of the NaBr. Tests of the activity of the helium from the cyclotron target chamber show that practically none of the radioactive gases is lost from the crystals. The separation of the target, therefore, involves breaking up the crystal lattice of the salt to release the gases. If the sodium bromide crystals are placed in a monel metal tube and melted, the released gas can be shown to contain radioactive krypton free from measurable amounts of radioactive bromine.

Since the number of radioactive bromine atoms is so much smaller than the number of inactive bromine atoms in the NaBr, and equilibrium exists, the number of radioactive bromine atoms free from the NaBr is completely negligible. The fact that exchange is responsible for the separation of the radioactive krypton from the radioactive bromine can be demonstrated in the following manner. Radioactive bromine gas is placed in contact with inert NaBr crystals for ten or fifteen minutes. The bromine gas is then pumped off, and the NaBr crystals are baked and pumped for twelve hours. At the end of this time, if the NaBr is tested for activity, it will be

* Department of Physics.
† Research Laboratory of Inorganic Chemistry.
[1] M. S. Livingston, J. App. Phys. **15**, 2, 128 (1944).
[2] A. H. Snell, Phys. Rev. **52**, 1007 (1937); E. P. Clancy, Phys. Rev. **58**, 88 (1940); E. C. Creutz, L. A. Delsasso, R. B. Sutton, M. G. White, and W. H. Barkas, Phys. Rev. **58**, 481 (1940).

found that the activity which was present in the bromine gas is now to be found in the NaBr crystals.

The apparatus for the separation of the krypton therefore consists merely of a vessel in which the NaBr may be melted, fitted with inlet and outlet tubes so that the gas may be swept from the vessel. NaBr melts at 755°C, and, therefore, a container must be used which will stand this temperature. Quartz would stand the temperature and would be convenient, since we can see when the NaBr is melted. Unfortunately, however, quartz is attacked by the molten NaBr and shatters after a few separations. Monel metal has been found to stand up as a fusion vessel for the crystals. A hot-rolled monel metal rod 10 inches long and $1\frac{1}{4}$ inches in diameter is drilled out to form a tube closed at one end. The open end is turned to a standard taper and ground to fit the male part of a Pyrex glass ground joint. A few turns of $\frac{1}{4}$-inch copper tubing are soft-soldered onto the upper end of the tube as cooling coils for the grind. A sketch of the apparatus is shown in Fig. 1. The bombarded crystals are placed in the bottom of the tube and the apparatus is evacuated with a mechanical vacuum pump. If the krypton gas is to be swept into an evacuated flask this may be connected to the outlet of the apparatus and both the flask and the monel metal apparatus evacuated together. The metal tube is tipped to an angle of about thirty degrees to the horizontal. The bottom end containing the crystals is heated in a large soft oxygen flame to a bright red heat and kept there for about five minutes. Water running through the cooling coils keeps the grease in the ground joint from getting hot. After the NaBr is melted under a vacuum it is allowed to cool, and the released krypton gas is swept into an evacuated bulb by letting any convenient sweeping gas in through the inlet going to the bottom of the metal vessel.

SOLUTION METHOD

Sodium bromide was chosen for bombardment for this separation method also, not only because of its high bromine content and relatively small tendency to be hygroscopic, but also on account of its high solubility.

Preparation of the Target

Although the crystalline reagent salt is soluble, its rate of solution is slow. The salt is fused in a nickel crucible and the melt poured into a porcelain dish. When cool it is ground in a mortar, and a fine powder is obtained which dissolves quickly. Because the total activity of the target is high, this high rate of solution is necessary to reduce the time of handling. A slight tendency to cake has been observed with this fused powder. This is minimized by preparing small quantities (40 g), drying the final powder at 150°C for several hours, and bottling and sealing while warm.

Separation of the Target

The apparatus used for this method of separation is shown in Fig. 2. The bombarded NaBr

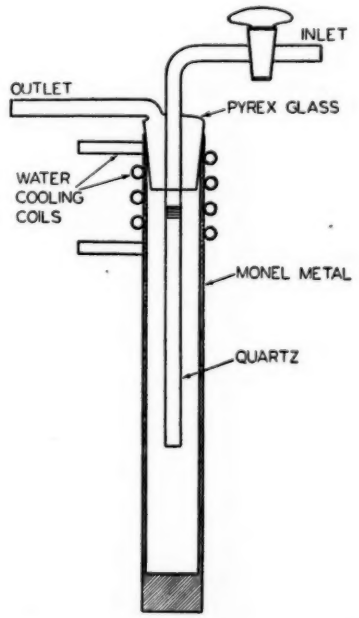


FIG. 1. Apparatus for the fusion method of separation.

is placed in the part of the apparatus marked *A* through the ground joint at the top. The stopcock between parts *A* and *B* is closed. The part of the apparatus marked *B* (volume of 70 cc) is filled two-thirds full with a solution of 0.01*M* in NaOH. The whole apparatus is then evacuated to the vapor pressure of the solution with a mechanical vacuum pump. After the apparatus

is pumped down, all the stopcocks are closed. Opening the stopcock between the parts of the apparatus *A* and *B* will allow the target material to fall into the solution. If the powdered NaBr has taken on a little water, the material may not

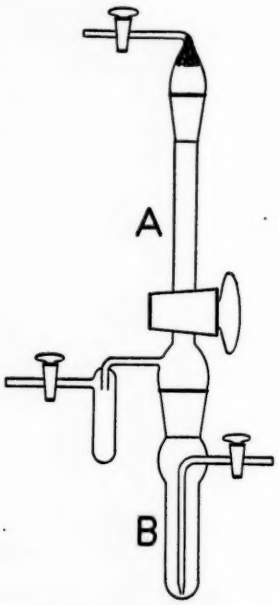


FIG. 2. Apparatus for the solution method of separation.

fall down easily, in that case either tapping or letting in a small amount of gas through the stopcock at the top will drive the powder down into the solution.

Although NaBr is quite soluble in water, shaking the mixture will greatly increase the rate of solution of the crystals. Since the whole apparatus is at reduced pressure, there is no danger that the ground joints will come apart and the whole apparatus can be taken up and shaken vigorously until the crystals are all dissolved.

Dissolving the sodium bromide removes the gases from the crystals by destroying them. The radioactive bromine is held in solution by the exchange phenomenon discussed in the fusion separation method. The purpose of the NaOH is to insure the absence of HBr in the gaseous phase above the liquid. The only remaining step is to get the krypton out of the solution. This can be done mechanically by sweeping gas through the solution. If the krypton is to be collected in a bulb, the evacuated bulb can be connected by rubber tubing to the stopcock to the left of part *B* in Fig. 2. If air is used as a sweeping gas, the stopcock to the left of part *B* is first opened and then the stopcock to the right is opened slowly. As the air bubbles through the solution, it will carry along the krypton gas. If gas other than air is used, so that it comes from a high pressure tank, a manometer must be included in the system so that the apparatus will not be filled to greater than atmospheric pressure.

To collect the gas in a very small volume, the krypton can be swept into an evacuated bulb with carbon dioxide. This gas can then be absorbed with fused sodium hydroxide and the krypton forced into a capillary side tube by displacement with mercury.

Yield

Rough measurements of the yield of the 34-hour krypton isotope have been made. Using the preparation and either separation method just described the gas was swept into an evacuated bulb. The krypton intensity measurements were made by placing the bulb containing the radioactive krypton three meters from a platinum screen cathode Geiger-Müller counter. The counter was covered by 1.1 mm of lead. All activity data were obtained by comparison with calibrated radium standards.

TABLE I.

$\frac{\text{Mg Ra } \gamma\text{-ray equiv.}}{\mu \text{ amp. hr.}}$	Mev
0.03	12
0.06	13
0.13	14

Table I gives the measured thick target yields for the 34-hour krypton isotope; the number of milligrams radium gamma-ray equivalents per microampere hour beam is given for three corresponding values of the measured beam current energy.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 4 APRIL, 1944

An Approximate Relation Between Surface Tension and Concentration for Regular Solutions

M. WALES
General Laboratories, U. S. Rubber Company, Passaic, New Jersey
(Received January 7, 1944)

An equation for the variation of surface tension with concentration in regular solutions is derived using Hildebrand's model and calculating the work per unit interfacial area required to separate a body of liquid reversibly into two infinitely removed parts. Spherical symmetry in shape and molecular field of both components is assumed. Values of a factor of deviation from the geometric mean relationship for intermolecular attraction between unlike non-polar molecular species are calculated both from surface tension and vapor pressure data. Values of the factor calculated from these two independent sources for a number of systems are in reasonable agreement. The linearity of surface tension with volume fraction in ideal systems is predicted, in agreement with experiment.

I. INTRODUCTION

HILDEBRAND[1] has derived an equation for partial molal heats of solution in non-polar binary systems on the assumptions of spherical symmetry of the two molecular species, geometric mean interaction between unlike molecules, and neglect of repulsion potentials. The same relation has also been obtained from different postulates.[2,3]

In this paper equations for the variation of surface tension with concentration will be derived using Hildebrand's model and the calculation by Margenau[4] of the "total surface energy" of a pure liquid. Margenau's result is considered by Kassel and Muskat[5] to represent more nearly the free surface energy or surface tension.

If a column of liquid is reversibly separated into two parts, the work per unit interfacial area necessary to accomplish the separation of the parts to infinity is equal to twice the free surface energy, while the sum of the work required and the heat absorbed per unit interfacial area during this process is equal to twice the total surface energy.

Kassel and Muskat[5] calculated the potential energy of one-half of an infinite body of liquid with respect to the other half and considered this to be the increase in total surface energy when the two parts were separated to infinity. This corresponds to the work done in an irreversible separation, and as they admitted, all that can be rigorously stated about the quantity calculated in this manner is that it is greater than the surface tension and less than the total surface energy. However, arguments were advanced to show that it corresponded more nearly to the total surface energy than to the free surface energy.

Margenau,[4] on the other hand, calculated the force exerted by one-half of the liquid upon the other as a function of the distance of separation between halves and formed $\int_0^\infty Fxdx$ to obtain the work required in the separation. According to Kassel and Muskat this represents an approach to an equilibrium process and the quantity obtained should be very nearly equal to twice the surface tension.

In the following calculations, emphasis should be placed on the fact that the validity of the relationships deduced does not depend on the equality of Margenau's equation to the surface tension, but only upon its proportionality, provided the constants of proportionality are the same for the mixture and both components. In addition to the postulates of Hildebrand, the effect of the vapor phase is neglected, as well as that of differences in bulk and surface concentration, on the force of attraction between halves during separation. The neglect of the vapor phase should not affect the form of the relationship

[1] J. H. Hildebrand, *Solubility* (Reinhold Publishing Company, New York, 1936), second edition, pp. 69–73.
[2] J. J. Van Laar, Zeits. f. physik. Chemie **A137**, 421 (1928).
[3] G. Scatchard, Chem. Rev. **8**, 321 (1931).
[4] H. Margenau, Phys. Rev. **38**, 365 (1931).
[5] L. S. Kassel and M. Muskat, Phys. Rev. **40**, 627 (1932).

obtained appreciably at low pressures. Examination of the data for mercury[6] in air and in vacuum shows that its surface tension is not changed by a large percentage by the presence of air. Also the surface tension of organic liquids in general is not very much different in air and at low pressures of saturated vapor. In any case the variation in the difference with concentration would be small. Neglecting differences in bulk and surface concentrations should not invalidate the results for the class of mixtures considered, where the rate of change of surface tension with concentration is not excessive.

II. GENERAL DERIVATION

Consider two infinite bodies of liquid with parallel plane surfaces, each containing n_1 mole fraction of species (1) and n_2 mole fraction of species (2), with the surfaces separated by a distance x.

The volume of the element between r and $r+dr$ and z and $z+dz$ is

$$\frac{2\pi r dz dr}{\cos\theta}. \tag{1}$$

See Fig. 1. Assume a molecule of (1) to be at the point P. The total force exerted on it by the molecules of (1) in the above-mentioned annular element, along the normal to the surfaces, is

$$\frac{2\pi N n_1 r W_{11}}{V}\left(\frac{\partial E_{11}}{\partial z}\right)dz dr, \tag{2}$$

where E_{11} and W_{11} represent the potential and radial distribution functions, respectively, between species (1), N the Avogadro number, and V the molal volume of the mixture.

Likewise the force exerted on a molecule of (1) at P by the molecules of (2) in the annulus is

$$\frac{2\pi N n_2 r W_{12}}{V}\left(\frac{\partial E_{12}}{\partial z}\right)dz dr, \tag{3}$$

where the significance of the symbols is analogous to those in (2). Similar expressions follow for a molecule of (2) at P. Since per unit area on the right-hand side there are $(N/V)n_1 dy$ molecules

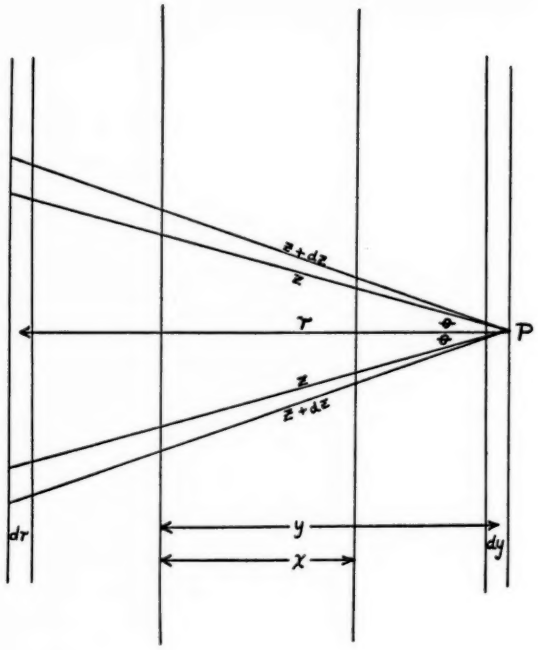


FIG. 1.

of (1) and $(N/V)n_2 dy$ molecules of (2) in the element of thickness dy, we obtain for the total force exerted by the annular element upon the element dy per unit area

$$2\pi\left(\frac{N}{V}\right)^2 r\left[n_1^2 W_{11}\left(\frac{\partial E_{11}}{\partial z}\right)+n_2^2 W_{22}\left(\frac{\partial E_{22}}{\partial z}\right)+2n_1 n_2 W_{12}\left(\frac{\partial E_{12}}{\partial z}\right)\right]dz dr dy. \tag{4}$$

Summing this from $z=r$ to $z\to\infty$ gives the force per unit area exerted on the thin sheet of thickness dy by a thin sheet of thickness dr in the opposite body of liquid.

Further summation from $r=y$ to $r\to\infty$ and from $y=x$ to $y\to\infty$ gives the force exerted by one body of liquid upon the other per unit area.

Then

$$\gamma=\tfrac{1}{2}\int_0^\infty F_x dx, \tag{5}$$

where F_x is the force exerted by one body of liquid upon the other per unit area at any separation x.

[6] *International Critical Tables*, first edition, Vol. IV, p. 440 (1928).

Therefore, from (4),

$$\gamma=\pi\left(\frac{N}{V}\right)^2\int_0^\infty\int_x^\infty\int_y^\infty\int_r^\infty r\Big[n_1^2W_{11}\left(\frac{\partial E_{11}}{\partial z}\right)+n_2^2W_{22}\left(\frac{\partial E_{22}}{\partial z}\right)+2n_1n_2W_{12}\left(\frac{\partial E_{12}}{\partial z}\right)\Big]dzdrdydx. \quad (6)$$

Now for either pure component it can be shown in a similar manner that

$$\gamma_{1,2}=\pi\left(\frac{N}{V_{1,2}}\right)^2\int_0^\infty\int_x^\infty\int_y^\infty\int_r^\infty rW_{11,22}\times\left(\frac{\partial E_{11,22}}{\partial z}\right)dzdrdydx. \quad (7)$$

V_1 and V_2 are the molal volumes of the pure components. Substituting (7) into (6) gives the following relation:

$$\gamma=\frac{n_1^2V_1^2\gamma_1}{V^2}+\frac{n_2^2V_2^2\gamma_2}{V^2}+\frac{c'n_1n_2}{V^2}. \quad (8)$$

The quantity C' in the last term contains the function W_{12} which on the basis of Hildebrand's postulates is independent of concentration. This factor should therefore be a constant at constant temperature, and could also be written

$$C'=CV_1V_2. \quad (9)$$

Equation (8) then becomes

$$\gamma=v_1^2\gamma_1+v_2^2\gamma_2+cv_1v_2, \quad (10)$$

where v_1 and v_2 are fractions by volume, provided the volume of the solution is additive from the volumes of the constituents. This is very nearly the case for the mixtures considered.

A similar relation was proposed by Poisson:[7]

$$h\rho=(h\rho)_1v_1^2+(h\rho)_2v_2^2+fv_1v_2, \quad (10a)$$

where h is the capillary rise and ρ the density and f is a constant. This is identical with (10) only when the angles of contact for both components and the solution are equal.

[7] S. D. Poisson, *Theorie de l'action capillaire* (Paris, 1831). See W. H. Whatmough, Zeits. f. physik. Chemie **39**, 129 (1902).

By making use of certain simplifying assumptions, it is possible to evaluate roughly the constant C in terms of other properties of the mixture under consideration.

Returning to Eq. (6), it can be seen that C is equal to

$$\frac{2\pi N^2}{V_1V_2}\int_0^\infty\int_x^\infty\int_y^\infty\int_r^\infty rW_{12}\left(\frac{\partial E_{12}}{\partial z}\right)dzdrdydx. \quad (11)$$

It can also be shown by repeated integration that

$$\gamma_{1,2}=\frac{\pi}{8}\left(\frac{N}{V_{1,2}}\right)^2\int_0^\infty z^4\left(\frac{\partial E_{11,22}}{\partial z}\right)W_{11,22}dz. \quad (12)$$

If it is assumed that $E(Z)=-k/z^6$ (neglecting the repulsion potential), (12) becomes

$$\gamma_{1,2}=\frac{3}{4}\pi\left(\frac{N}{V_{1,2}}\right)^2k_{1,2}\int_0^\infty\frac{W_{11,22}}{z^3}dz. \quad (12a)$$

By assuming with Hildebrand[8] that all the W functions are the same functions of that value of z at which their first maximum occurs the integrals for the pure components (12a) may be transformed to (13), where the integrand is the same for both components.

$$\frac{3}{4}\left(\frac{N}{V_{1,2}}\right)^2\frac{\pi k_{1,2}}{z_{1,2}^2}\int_0^\infty\left(\frac{z_{1,2}}{z}\right)^3f\left(\frac{z}{z_{1,2}}\right)d\left(\frac{z}{z_{1,2}}\right). \quad (13)$$

z_1 or z_2 and k_1 or k_2 are the above-mentioned values of z and the force constants k for the components.

This is equivalent to assuming that the structure of each pure component liquid is essentially the same except for differences in molecular size. How nearly justified this is for actual non-polar liquids is a debatable question. However, mercury and gallium[8] obey this assumption very closely, as would be expected, since they are spherical molecules.

Putting the expression (11) for C into the form (13) we have

$$C=\frac{3}{4}\frac{\pi N^2k_{12}}{z_{12}^2V_1V_2}\int_0^\infty\left(\frac{z_{12}}{z}\right)^3f\left(\frac{z}{z_{12}}\right)d\left(\frac{z}{z_{12}}\right), \quad (14)$$

where z_{12} is the value of z at which the function

[8] J. H. Hildebrand, *Solubility*, second edition, p. 72.

W_{12} has its first maximum and k_{12} is the force constant for the potential function between unlike molecules [$E_{12}(Z) = -k_{12}/Z^6$ neglecting the repulsion potential as before].

Hildebrand assumed that $k_{12} = (k_1 k_2)^{\frac{1}{2}}$. This expression was derived from wave mechanical considerations[9] and represents the upper limit for the dispersion effect between unlike molecules. In general, $k_{12} < (k_1 k_2)^{\frac{1}{2}}$. We shall write

$$k_{12} = s(k_1 k_2)^{\frac{1}{2}}, \tag{15}$$

where $s < 1$ and is a property of the system under consideration.

From (14), (15), and the expressions for the pure components (13), and remembering that all the integrands should be equal, we obtain

$$C = 2s(\gamma_1\gamma_2)^{\frac{1}{2}}\left(\frac{z_1 z_2}{z_{12}^2}\right). \tag{16}$$

The expression involving the z's is only slightly different from unity even when the respective values differ by as much as 50 percent. Therefore, it would be expected that C would be equal to or less than $2(\gamma_1\gamma_2)^{\frac{1}{2}}$ since $S \leqq 1$. This is in agreement with experiment.

It would also be expected that the greater the deviation from the value $2(\gamma_1\gamma_2)^{\frac{1}{2}}$ the greater would be the deviation of the constant

$$D^2 = \left[\left(\frac{\Delta E}{V}\right)_1^{\frac{1}{2}} - \left(\frac{\Delta E}{V}\right)_2^{\frac{1}{2}}\right]^2 \tag{17}$$

in the Van Laar-Scatchard-Hildebrand equation for activity coefficients of regular solutions from its value calculated from vapor pressure data. This follows from the fact that k_{12} was assumed to be equal to $(k_1 k_2)^{\frac{1}{2}}$ in obtaining the constant D^2 in this form. Any departure from this leads to a difference in the values obtained from vapor pressures and those calculated from (17).

The relationship between C and D^2 will now be put in a semiquantitative form. The internal latent heat of vaporization of a non-polar liquid is

$$\Delta E = \frac{2\pi N^2 k}{V}\int_0^\infty E(z) W z^2 dz \tag{18}$$

without regard to sign.

[9] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930). F. London, *ibid.* **63**, 245 (1930); Zeits. f. physik. Chemie **B11**, 222 (1930).

Making the assumptions in (12a) through (15), applying them to (18), and having also the relation[10]

$$D^2 = 2\pi N^2\left[\frac{2k_{12}}{V_1 V_2}\int_0^\infty \frac{W_{12}}{z^4}dz - \frac{k_1}{V_1^2}\int_0^\infty \frac{W_{11}}{z^4}dz - \frac{k_2}{V_2^2}\int_0^\infty \frac{W_{22}}{z^4}dz\right], \tag{19}$$

we obtain

$$D_p^2 = \left\{\left(\frac{\Delta E}{V}\right)_1 + \left(\frac{\Delta E}{V}\right)_2 - 2s\left(\frac{[z_1^3 z_2^3]^{\frac{1}{2}}}{z_{12}^3}\right)\left[\left(\frac{\Delta E}{V}\right)_1\left(\frac{\Delta E}{V}\right)_2\right]^{\frac{1}{2}}\right\}, \tag{20}$$

where D_p^2 should now be equal to the value obtained from vapor pressures since deviations of k_{12} from $(k_1 k_2)^{\frac{1}{2}}$ have been taken into account. The s factor, naturally, should be the same as in Eq. (16). The factor involving the z's is also always fairly close to unity, although not equal to that in (16). Lumping this factor together with s, (16) and (20) can be rewritten

$$C = 2S_\gamma(\gamma_1\gamma_2)^{\frac{1}{2}}, \tag{16a}$$

$$D_p^2 = \left\{\left(\frac{\Delta E}{V}\right)_1 + \left(\frac{\Delta E}{V}\right)_2 - 2S_p\left[\left(\frac{\Delta E}{V}\right)_1\left(\frac{\Delta E}{V}\right)_2\right]^{\frac{1}{2}}\right\}, \tag{20a}$$

where S_γ and S_p should be nearly equal, or at least of the same order of magnitude and both equal to or less than unity. In view of the approximations involved, it seems rash to predict whether one or the other will be greater, on the basis of the z terms.

III. IDEAL SOLUTIONS

Some conclusions can be drawn from (16a) and (20a) with regard to the surface tension—concentration relationship in ideal solutions.

For all the systems of the type discussed, γ_1 and γ_2 are near enough together so that $2(\gamma_1\gamma_2)^{\frac{1}{2}} = \gamma_1 + \gamma_2$ without appreciable error. (See experimental data and calculations.) When $C = \gamma_1 + \gamma_2$, Eq. (10) reduces to

$$\gamma = v_1\gamma_1 + v_2\gamma_2. \tag{21}$$

[10] J. H. Hildebrand, *Solubility*, second edition, p. 71.

TABLE I.*

System	S_γ	S_p	Int. pressure	t°C	D^2 Vapor pressure	t°C
CCl_4-benzene 50°C	0.96	0.994[a]	0.22	25°C	0.92	50°C
Benzene-cyclohexane 25°C	0.95–0.98	0.986[b]	0.96	79°C	2.19	79°C
Benzene-ethylene chloride 17°C	0.96–0.98	1.00[c]	0.07	25°C	0	—
50°C	1.00	1.00	—			
CS_2-benzene 20°C	0.85–0.92	0.99[d]	1.0	25°C	3.24	25°C
CS_2-benzene 30°C	0.86–0.81	0.99	1.0	25°C	3.24	25°C
Benzene-napthalene 79.5°	1.00	1.00[e]	0.36	25°C	0	79.5°C
Benzene-toluene 10.8°	1.00	1.00[f]	0.35	25°C	0	80°C

* All internal pressures were taken from Hildebrand, *Solubility*, second edition, pp. 104–105.
[a] J. V. Zawidzki, Zeits. f. physik. Chemie **35**, 129 (1900).
[b] J. H. Hildebrand, *Solubility*, second edition, p. 124.
[c] See reference 17.
[d] J. Sameshima, J. Am. Chem. Soc. **40**, 1503 (1918).
[e] A. N. Campbell, Can. J. Research **B19**, 143 (1941).
[f] See reference 16.

TABLE II. Tabulated data and calculations. All values of γ in dynes/cm. Benzene-ethylene dichloride.*

Vol. % ethylene chloride	γ 17°C	C Calc. 17°C	γ Calc. 17°C $C=59.5$	γ Calc. 17°C linear relation	γ 50°C	γ Calc. 50°C linear relation
0	29.17	—	—	—	24.08	—
10	29.33	59.9	29.30	29.42	24.38	24.38
20	29.50	59.8	29.46	29.67	24.66	24.67
30	29.61	59.3	29.64	29.92	24.98	24.99
50	30.05	59.4	30.09	30.42	25.56	25.56
70	30.53	59.0	30.64	30.93	26.16	26.16
90	31.21	58.5	31.30	31.42	26.75	26.75
100	31.68	—	—	—	27.05	—
		$\gamma_1+\gamma_2$ at 17°C = 60.9	$C \leqq 59.5$	$2(\gamma_1\gamma_2)^{\frac{1}{2}}=60.8$		

* Yajnik, Sharma, and Bharadway, Quart. J. Ind. Chem. Soc. **3**, 63 (1926). Volume fractions calculated by the authors.

TABLE III. Carbon tetrachloride-benzene 50°C.*

Mole % benzene	Vol. % benzene	γ	C	γ calc. $C=47.0$
0	0	22.98	—	—
20.19	20.28	23.21	46.8	23.23
35.32	33.75	23.47	47.2	23.45
52.88	51.15	23.78	47.0	23.78
67.85	66.30	24.09	47.0	24.09
81.85	80.80	24.39	46.6	24.45
100.00	100.00	24.98	—	—
	Densities—Benzene = 0.8372		$\gamma_1+\gamma_2=48.0$	
	Carbon tetrachloride = 1.537		$2(\gamma_1\gamma_2)^{\frac{1}{2}}=48.0$	
			$C \leqq 47.0$	

* J. W. Belton, Trans. Faraday Soc. **31**, 1642 (1935).

This relation was proposed by Volkmann.[11] In other words, when $S_\gamma=1$, Eq. (21) would be expected to hold.

It is an experimental fact that when for non-polar liquids, $(\Delta E/V)_1=(\Delta E/V)_2$ the mixture is ideal, and $D_p^2=0$. In this case, from Eq. (20a) it is obvious that $S_p=1$. Now, since $S_\gamma \leqq S_p$ it is highly probable that Eq. (21) will hold, although it is possible that S_γ may be slightly less than unity, leading to negative deviations of the surface tension from this linear relation. In other words, when vapor pressure is linear in mole fraction, surface tension can reasonably be expected to be linear in volume fraction. This subject will be discussed at greater length in the next section.

[11] Volkmann, Ann. d. Physik [3] **16**, 321 (1882).

TABLE IV. Benzene-napthalene 79.5°C.*

Wt. % napthalene	Molal volume of mixture cc	Vol. % napthalene	γ	Linear relation[a]
0	95.7	0.00	27.80[b]	—
10	98.3	8.41	29.20	29.08
20	100.9	17.15	30.44	30.40
30	103.4	26.10	31.70	31.70
40	105.9	35.50	33.00	33.06

* A. N. Campbell, Can. J. Research **B19**, 143 (1941).
[a] Read off a straight line through the experimental points on a plot of γ *versus* v.
[b] There is obviously an error of method here. The I.C.T. value at 80° is 21.26 dynes/cm.

TABLE V. Benzene-cyclohexane 25°C.*

Mole % benzene	Vol. % benzene	γ	C	γ calc. $C=51.0$	
0.00	0.00	24.35[a]	—	—	
37.03	32.92	25.36	51.5	25.27	$\gamma_1+\gamma_2=52.7$
47.60	42.77	25.65	51.0	25.65	$2(\gamma_1\gamma_2)^{\frac{1}{2}}=52.6$
54.92	50.06	25.84	50.7	25.91	$C\leqq 51.0$
70.37	66.15	26.41	50.2	26.60	
100.00	100.00	28.32	—	—	

Densities—Benzene 0.8734
Cyclohexane 0.7743

* D. L. Hammick and L. W. Andrew, J. Chem. Soc. **132**, 754 (1929).
[a] Interpolated value from the data of M. Hennaut-Roland and L. Lek, Bull. Soc. Chim. Belg. **40**, 177 (1931). See *Annual Tables of Physical Constants*, Section 700(c), p. 4 (1941).

TABLE VI. Benzene-toluene 10.8°C.*

Mole % benzene	γ	Vol. % benzene	γ from linear relation
0	29.61	0	—
24.98	29.76	24.7	29.74
50.07	29.85	49.5	29.86
75.06	30.02	74.6	29.98
100.00	30.11	100.0	—

Densities—Benzene 0.8885
Toluene 0.8742

* J. L. R. Morgan and M. A. Griggs, J. Am. Chem. Soc. **39**, 2261 (1917). See also *International Critical Tables*, first edition, Vol. IV, p. 473 (1928).

TABLE VII. Carbon disulfide-benzene.*

Mole % benzene	γ 20°C	γ 30°C	Vol. % benzene	C Calc. 20°C	C Calc. 30°C	γ 20°C $C=55.0$ Calc.	γ Calc. 30°C $C=50.0$
0	32.38	30.91	0	—	—	—	—
7.89	31.04	29.69	11.21	52.0	50.1	31.36	29.69
16.84	30.20	28.82	22.99	53.4	51.0	30.48	28.62
28.23	29.56	283.6	36.69	54.5	52.8	29.56	27.75
46.47	29.04	27.75	56.39	55.6	48.8	28.90	26.96
63.81	28.94	27.55	72.20	56.6	47.0	28.64	26.80
100.00	28.89	27.52	100.00	—	—	—	—

Densities—Benzene = 0.8794
20°C carbon disulfide = 1.263
20° $\gamma_1+\gamma_2=61.3$
$2(\gamma_1\gamma_2)^{\frac{1}{2}}=61.2$

Densities—Benzene = 0.8678
30°C carbon disulfide = 1.248
30° $\gamma_1+\gamma_2=58.4$
$2(\gamma_1\gamma_2)^{\frac{1}{2}}=58.3$

* J. W. Belton, Trans. Faraday Soc. **31**, 1642 (1935).

TABLE VIII. Carbon disulfide-chloroform 18°C.*

Wt. % chloroform	Vol. % chloroform	γ	C	γ calc. $C=55.5$	
0	0	32.24	—	—	
20	17.49	30.59	54.0	30.81	$\gamma_1+\gamma_2=59.5$
40	36.13	29.53	55.5	29.53	$2(\gamma_1\gamma_2)^{\frac{1}{2}}=59.4$
60	55.99	28.42	55.3	28.47	$C\leqq 55.5$
80	77.25	27.78	55.7	27.74	
100	100.00	27.33	—	—	

Densities—Chloroform 1.493
Carbon disulfide 1.266

* W. H. Whatmough, Zeits. f. physik. Chemie **39**, 129 (1902).

IV. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS

To sum up the preceding deductions, it has been shown that the surface tension of a regular solution would be expected to obey the equation

$$\gamma=v_1^2\gamma_1+v_2^2\gamma_2+cv_1v_2.* \qquad (10)$$

The constant C would be expected to vary with each specific system, being in general $\leqq 2(\gamma_1\gamma_2)^{\frac{1}{2}}$. This would give either zero or negative deviations of the surface tension from the linear relation

$$\gamma=v_1\gamma_1+v_2\gamma_2, \qquad (21)$$

this relation holding for ideal systems. These conclusions are in agreement with experiment. It has been observed[12–14] that when the system is ideal the surface tension is linear in volume fraction and when the vapor pressure shows positive deviations from Raoult's law, the surface tension shows negative deviations from Eq. (21), and vice versa. Since all regular solutions show positive deviations from ideality, the theoretical relations are in harmony with these facts. The case of negative deviations from Raoult's law does not pertain to the theory developed, but positive deviations from the linear surface tension relation would be expected since $C>2(\gamma_1\gamma_2)^{\frac{1}{2}}$ due to chemical bonding or strong dipole attraction. Naturally Eq. (10) would not hold, with C varying with concentration.

Quantitatively, all the surface tension—concentration data found in the literature by the author for regular solutions can be fitted by Eqs. (10) or (21), with the exception of that for carbon disulfide-benzene. Equation (10) gives a minimum which does not exist. This error may be caused by a neglect of the difference between surface and bulk concentration in the derivation, but is probably due to orientation of the asymmetric CS_2 molecules in the interface. This system agrees with the vapor pressure equation for regular solutions fairly well.[15] In all cases for the non-ideal systems the constant C varies slightly with concentration. Nearly always there is a definite slight drift, but not enough to invalidate the equation except for CS_2-benzene.

For the ideal systems benzene-napthalene and benzene-toluene the surface tension is linear in volume fraction, as would be expected.

For ethylene dichloride-benzene at 50°C, surface tension is linear in volume fraction. At 17°C, it shows slight negative deviations. This system behaves ideally over this range.[16] The behavior at 17°C is theoretically possible from differences in S_γ and S_p.

Some objection might be raised as to whether this system constitutes a legitimate test of the theory, on account of the dipole moment of ethylene dichloride. However, the internal pressures of benzene and ethylene dichloride are, respectively, 80.9 and 82.3 cal./cc at 25°C[17] at which temperature the mixture is ideal, in agree-

* A relation of similar form might also hold for non-regular non-polar mixtures (i.e., one or both components a normal long chain hydrocarbon) with modifications, considering each "submolecule" in the chain as a molecule. However, this discussion is concerned only with regular solutions and it would be beyond the scope of this paper to discuss this possibility.

[12] R. P. Worley, J. Chem. Soc. **105**, 273 (1914).

[13] Yajnik, Sharma, and Bharadway, Quart. J. Ind. Chem. Soc. **3**, 63 (1926).

[14] O. Faust, Zeits. f. anorg. allgem. Chemie **54**, 61 (1926).

[15] J. H. Hildebrand, *Solubility*, second edition, p. 125.

[16] *International Critical Tables*, first edition, Vol. III, p. 287 (1928).

[17] Hildebrand, *Solubility*, "Table of internal pressure," second edition, p. 105.

ment with D^2 calculated from these values. Apparently the dipole effect is very small compared with the dispersion effect in its contribution to intermolecular attraction. The system carbon disulfide-chloroform also has a polar component, but behaves at least in qualitative accord with internal pressure differences.[18] This system was included because of this and the paucity of data available. There are more results in the literature for surface tensions of non-polar mixtures than are given here, but they were not used since they gave "shotgun curves" when plotted against concentration.

With regard to the factors S_γ and S_p, the values calculated from surface tension data and those from vapor pressures do not differ a great deal. The vapor pressure values are the larger. Values obtained where data were available are tabulated below (see Tables I–VIII). In calculating S_p values of internal pressures at the temperature in the fourth column and values of D^2 at the temperature in the sixth column were used.

In calculating volume fractions in all cases except where otherwise shown, the densities used were obtained from the equations of the *International Critical Tables*.[19]

ACKNOWLEDGMENTS

The author is indebted to Dr. Arthur E. Martell of Clark University, Worcester, Massachusetts, for suggestions which led to this work; to Dr. John B. Sampson of Clark University for criticism; and to the United States Rubber Company for permission to publish this paper.

[18] Hildebrand, *Solubility*, second edition, p. 127.

[19] *International Critical Tables*, first edition, Vol. III, p. 28 (1928).

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

The Steady-State Approximation in Polymerization Kinetics*

W. H. STOCKMAYER

Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

March 6, 1944

IT is customary in discussing the kinetics of vinyl polymerization to assume that the Bodenstein steady-state method can be used to calculate the concentration of the free radical intermediates with sufficient accuracy at all measurable extents of reaction,[1,2] and this assumption seems to be supported by the experimental data. Numerical estimates of the specific rates of individual steps in the polymerization mechanism, if based on the steady-state approximation, must conform to certain restrictions imposed by this assumption. Apparently it has not always been realized that such restrictions depend intimately on the kinetic details of the mechanism, so that conclusions reached from the extensive calculations of Ginell and Simha,[3] for example, cannot be applied without modification to a mechanism which differs from theirs. The intent of this letter is, therefore, to supply a brief discussion of the steady-state approximation for the currently accepted polymerization mechanism.[1,2]

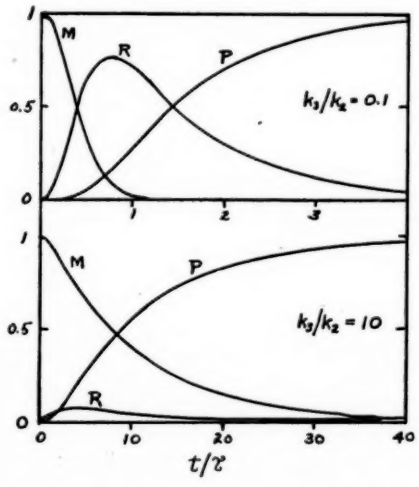


FIG. 1. Distribution of substrate among growing radicals, stable polymer, and unreacted monomer. R = radicals, P = polymer, M = monomer.

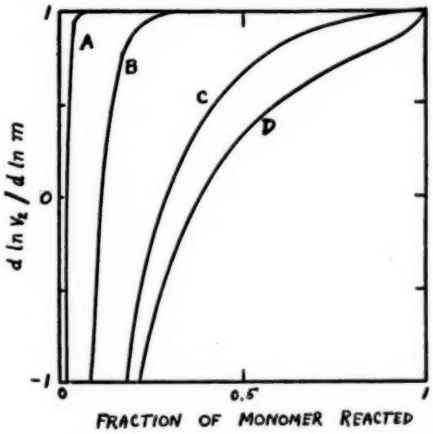


FIG. 2. Instantaneous apparent order ($d \ln v_2/d \ln m$) of polymerization reaction. Values of k_3/k_2 shown are: A, 100; B, 10; C, 1; D, 0.1.

Let the rates of initiation, propagation, and termination be v_1, v_2, v_3, respectively; let m be the concentration of monomer and r that of the free radicals. Then[1,2] $v_2 = k_2 mr$ and $v_3 = k_3 r^2$. The detailed form of v_1 need not be specified. The time-dependence of r is given by

$$dr/dt = v_1 - k_3 r^2. \tag{1}$$

If it be assumed *a priori* that the steady state is attained before appreciable polymerization occurs, Eq. (1) may be integrated on the assumption that v_1 is constant, to yield

$$r = (v_1/k_3)^{\frac{1}{2}} \tanh (t/\tau), \tag{2}$$

where $\tau = (k_3 v_1)^{-\frac{1}{2}}$. For $t \gg \tau$, r approaches its steady-state value of $(v_1/k_3)^{\frac{1}{2}}$ and τ becomes equal to the mean lifetime of the radicals.

Since $v_2 \gg v_1$ if high polymers are to be formed, the observed rate of monomer consumption is practically equal to the propagation rate v_2, which on the steady-state approximation becomes

$$v_2 = k_2 m (v_1/k_3)^{\frac{1}{2}}. \tag{3}$$

Whatever the detailed form of v_1, it is manifest from Eq. (3) that the half-life of the monomer has an order of magnitude

$$\tau_0 = k_2^{\frac{1}{2}}/v_1^{\frac{1}{2}} k_2. \tag{4}$$

If the steady-state assumption is justified for all measurable extents of polymerization, τ_0 must *a posteriori* be much larger than τ. But from Eqs. (2) and (4) this restriction can be written

$$\tau_0/\tau = k_3/k_2 \gg 1. \tag{5}$$

Superficially this result might seem to preclude the formation of high polymers, which demands $v_2 \gg v_3$; but because $r \ll m$ no contradiction is involved, since v_3 is of second order with respect to r. However, for the mechanism treated by Ginell and Simha[3] (for which $v_3 = k_3 mr$), just the inverse of Eq. (5) is required.

If v_1 is assumed to be independent of time throughout the whole polymerization (apparently a good approxi-

mation[1,2]), an exact analysis can be given which illustrates these points clearly, as the accompanying graphs show. In Fig. 1 the distribution of total substrate among growing radicals, stable polymer, and unreacted monomer is shown as a function of time for several values of k_3/k_2, and in Fig. 2 the instantaneous apparent order (defined as $d \ln v_2/d \ln m$) of the rate of monomer consumption is sketched as a function of the percentage of reacted monomer. As can be seen from Eq. (3), the steady-state approximation gives a first-order law.

The curves of Fig. 1 were obtained from the expressions:

$$m = m_0 \exp(-\varphi/\nu), \quad \text{(unreacted monomer)} \quad (6)$$
$$\Sigma n r_n = (m - m_0 e^{-\varphi})/(\nu - 1), \quad \text{(monomer in radicals)}$$

where $\varphi = \ln \cosh(t/\tau)$, $\nu = k_3/k_2$, and m_0 is the initial monomer concentration. The amount of stable polymer is found by difference. The apparent order is found to be

$$\frac{d \ln v_2}{d \ln m} = 1 - \frac{\nu}{(m_0/m)^{2\nu} - 1}. \quad (7)$$

Recently Mark and his co-workers[1] have estimated frequency factors of 10^5 and 10^4 liter/mole/sec. for k_2 and k_3, respectively, in the case of styrene, and have assigned to each rate an activation energy of 5 kcal./mole. Not only do these figures disobey Eq. (5), but the low frequency factors are difficult to explain. Since only the ratio $k_2/k_3^{\frac{1}{2}}$ can be obtained with any accuracy from experimental data, and since the estimated activation energies are not far from lower limits, a revision which satisfies both the experimental data and the dictates of Eq. (5) will necessarily give higher, more normal frequency factors for k_2 and k_3.

* Contribution No. 507 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

[1] See, for example, J. Abere, G. Goldfinger, H. Mark, and H. Naidus, Ann. N. Y. Acad. Sci. **44**, 267 (1943).

[2] C. C. Price, Ann. N. Y. Acad. Sci. **44**, 351 (1943).

[3] R. Ginell and R. Simha, J. Am. Chem. Soc. **65**, 706 (1943).

Some Light Scattering Experiments with High Polymer Solutions*

P. M. Doty, B. H. Zimm, and H. Mark

Columbia University, New York, New York and Polytechnic Institute of Brooklyn, Brooklyn, New York

March 6, 1944

Debye[1] has recently pointed out that light scattering in solutions of high polymers permits the determination of the slope of the osmotic pressure curve of such solutions and the molecular weight (weight average) of the solute.

Einstein,[2] Von Smoluchowski,[3] Gans,[4] and Raman and Ramanathan[5] give essentially the following equation for the turbidity of a colorless binary mixture due to fluctuations in density and concentration.

$$\tau = \frac{8\pi^3}{3\lambda^4 N_0}\left\{RT\beta\left[\rho\frac{\partial \epsilon}{\partial \rho}\right]^2 + \frac{M_1 c_2}{\rho\left(-\frac{\partial \ln f_1}{\partial c_2}\right)}\left(\frac{\partial \epsilon}{\partial c_2}\right)^2\right\}, \quad (1)$$

where τ = turbidity (extinction coefficient) units cm^{-1}, f_1 = fugacity of solvent, of molecular wt. M_1, $c_2 \doteq$ weight fraction of solute, $N_0 = 6.02 \times 10^{23}$, λ = wave-length of light in cm.

Assuming that β, the isothermal compressibility, is independent of concentration, the first term represents the turbidity due to fluctuations of the density ρ of the solvent. Thus if the turbidity of the solvent is subtracted from the measured turbidity of the solution, the remainder τ_2 will be, replacing ϵ by n^2, where n is the refractive index,

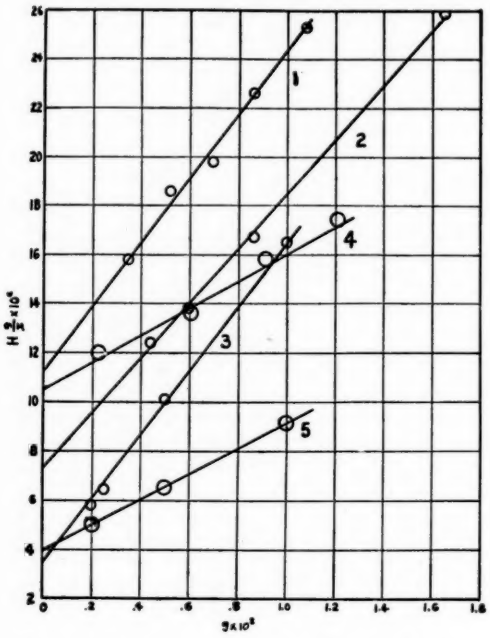


Fig. 1. Plot of $H(g_2/t_2)$ against g_2 for various samples of polystyrene in toluene and methylethyl ketone (see Table I).

$$\tau_2 = \frac{32\pi^3 M_1 c_2 n^2\left(\frac{\partial n}{\partial c_2}\right)^2}{3\lambda^4 N_0 \rho\left(-\frac{\partial \ln f_1}{\partial c_2}\right)}. \quad (2)$$

Recalling the relation

$$-\frac{\partial \ln f_1}{\partial c_2} = \frac{\bar{V}_1}{RT}\frac{\partial \pi}{\partial c_2}, \quad (3)$$

where π is the osmotic pressure, $\bar{V}_1$ the partial molal volume of solvent, and introducing g_2 (grams/cm^3) $= \rho c_2$, Eq. (2) becomes

$$\tau_2 = \frac{32\pi^3 g_2 n^2\left(\frac{\partial n}{\partial g_2}\right)^2}{3\lambda^4 N_0 \frac{1}{RT}\frac{\partial \pi}{\partial g_2}} \quad (4)$$

assuming $\bar{V}_1 = V_1 = M_1/\rho$.

TABLE I.

Graph No.	Os. Mol. Wt.	Turb. Mol. Wt.	Solvent
1	100,000	88,500	toluene
2	127,000	137,000	toluene
3	200,000	285,000	toluene
4	100,000	95,000	methylethyl ketone
5	200,000	250,000	methylethyl ketone

It has been found[6,7] that even for very low concentrations of high polymer solutions, it is necessary to use for the osmotic pressure:

$$\pi = RT\left(\frac{g_2}{M_2} + bg_2^2 + \cdots\right).$$

Equation (4) now becomes, with rearrangement,

$$\frac{g_2}{\tau_2} = \frac{3\lambda^4 N_0}{32\pi^3 n_1^2\left(\frac{\partial n}{\partial g_2}\right)^2}\left[\frac{1}{M_2} + \frac{2b_2}{RT}g_2 + \cdots\right] = \frac{1}{H}\left[\frac{1}{M_2} + \frac{2b_2}{RT}g_2 + \cdots\right]. \quad (5)$$

Hence a plot of $H(g_2/\tau_2)$ *versus* g_2 should give at low concentrations a straight line whose intercept is $1/M_2$.

We have made preliminary measurements of the turbidity of polystyrene fractions of known osmotic molecular weight[8] in two solvents. Our results, plotted in Fig. 1, show the expected linear relationship. The molecular weights obtained from the intercept are compared with the osmotic molecular weights in Table I.

Because of present experimental uncertainties, we attach no significance to the differences between the two methods of measurement. The slopes of the lines for the measurements in toluene agree within experimental error (30 percent) with the slopes calculated from the osmotic data[7] (samples 120° and 180°). Our measurements of refractive index (±0.00001) have shown that n varies linearly with g_2 over the concentration range used, and thus $(\partial n/\partial g_2)$ is considered a constant having a value 0.213 for polystyrene-methylethyl ketone and 0.102 for polystyrene-toluene (Na-D line).

In the above, we have not considered the scattering due to orientation fluctuation.[1,4,9] However, measurements of the depolarization showed that this contribution is small enough to neglect in this preliminary work.

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research at Columbia University.

[1] P. Debye, Lecture given in various Am. Chem. Soc. sections and at the rubber symposium of the American Physical Society in Chicago, November 12, 1943.
[2] A. Einstein, Ann. d. Physik **33**, 1275 (1910).
[3] M. Von Smoluchowski, Ann. d. Physik **25**, 205 (1908).
[4] R. Gans, Zeits. f. Physik **17**, 353 (1923).
[5] C. V. Raman and R. Ramanathan, Phil. Mag. [6] **45**, 213 (1923).
[6] M. L. Huggins, J. Am. Chem. Soc. **64**, 1712 (1942).
[7] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).
[8] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **65**, 2319 (1943).
[9] H. Mueller, Phys. Rev. **50**, 547 (1936).